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ABSTRACTS OF THE PROCEEDINGS

OF

THE CHEMICAL SOCIETY.

Vol. I. Nos. 1—15.

JANUARY—DECEMBER, 1885.

EDITED BY THE SECRETARIES.

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3	18	from top,	*for* A. J. Green	*read* A. G. Green
17	7	,, bottom,	,, Davis	,, Davies
46	1	,, top,	,, 36	,, 26
46	18	,, ,,	,, densities	,, boiling points
51	2	,, bottom,	insert By C. S. S. Webster	
77	5	,, top,	*for* James Bell, M.A.,	*read* James Bell, B.A., LL.M.
87	7	,, bottom,	,, "burnt"	,, burst.
92	20	,, ,,	,, ones, provided	,, ones. Provided
92	18	,, ,,	,, acid;	,, acid,
93	14	,, ,,	,, Shmidzu	,, Shimidzu
94	1	,, top	,, nitrous	,, nitric
96	16	,, bottom	,, $2(HONH_3)NO_2$	,, $2(HONH_3)NO_3$
97	1	,, top	,, anthraquinones	,, anthraquinone
99	16	,, bottom	,, Print	,, Prout
106	8	,, ,,	,, Metacinname	,, Metacinnamene
117	2	,, ,,	,, 13th	,, 10th
124	13	,, top	,, H_2O_3	,, H_2O_4
130	16	,, ,,	,, fractions	,, crystals

DATES OF ISSUE OF THE MONTHLY NUMBERS OF THE JOURNAL OF THE CHEMICAL SOCIETY TO FELLOWS.

January	number was issued	7th January.
February	,,	31st ,,
March	,,	28th February.
April	,,	1st April.
May	,,	2nd May.
June	,,	5th June.
July	,,	3rd July.
August	,,	1st August.
September	,,	1st September.
October	,,	7th October.
November	,,	31st ,,
December	,,	3rd December.
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LIST OF GRANTS MADE FROM THE RESEARCH FUND DURING THE YEAR.

£75 to Professor T. E. Thorpe: for the investigation of the relation between surface-tension and viscosity of liquids and their chemical nature.

£15 to Dr. A. B. Griffiths: for the continuation of his experiments on the use of ferrous sulphate as a manure.

£20 to Dr. J. W James: for the study of the homologues of taurine.

£20 to Dr. Hodgkinson: for the continuation of his investigation of fluorene and its derivatives.

£10 to Mr. G. Stallard: for the examination of certain bromonaphthalenesulphonic acids.

£20 to Mr. Thomas Turner: for the continuation of his experiments on the influence of silicon on the properties of iron and steel.

£25 to Dr. G. H. Bailey: for the examination of zirconium compounds with a view to the discovery of suitable means of determining the atomic weight of the element.

£50 to Dr. A. K. Miller: to investigate the products of the decomposition of solid paraffin by heat.

£10 to Mr. W. W. J. Nicol: in aid of an investigation of the nature of solution.

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Name.	Proposed.	Elected.
Adie, Richard Haliburton	November 5th ..	December 3rd.
Adriance, John Sabine	„ „	„ „
Aikman, Charles Morton	„ „	„ „
Alcock, Frank Harris	March 5th	May 7th.
Amphlett, E. Greenhill	February 5th ...	March 5th.
Anderson, James	November 5th ..	December 3rd.
Bell, William James	June 18th	November 19th.
Blades, Charles M.	January 15th ...	March 5th.
Blaine, R. Gordon	February 5th ...	„ „
Burnett, Joseph Fearon	May 7th	June 4th.
Cannon, Matthew	March 5th.....	May 7th.
Christopher, Robert G.	November 19th .	December 17th.
Clark, Edward Brown	„ 5th ..	„ 3rd.
Clarke, W. Lane	December 4th...	February 5th.
Cohen, Julius B.	January 15th...	March 5th.
Collie, J. Norman	December 4th...	February 5th.
Cousins, William J.	November 19th .	December 17th .
Davies, Frederick Mark	February 5th ..	March 5th.
Dechan, Martin	March 5th.....	May 7th.
De Köningh, Leonard	May 21st.....	June 18th.
De Souza, Edward	June 18th.....	November 19th.
Dixon, Augustus E.	December 4th ..	February 5th.
Dunstan, Malcolm J. R.	November 5th ..	December 3rd.
Dyson, Gibson	June 4th.....	November 19th.
Ellis, George E. R.	November 5th ..	December 3rd.
Embrey, George	December 4th...	February 5th.
Epps, James, junr.	November 5th ..	December 3rd.
Farmer, E. Howard	February 5th ...	March 5th.
Freear, Harvey M.	March 19th	May 7th.
Fletcher, Lazarus	November 5th ..	December 3rd.
Follows, Harold	March 19th	May 7th.
Gadd, William L.	November 5th ..	December 3rd.
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Gibson, Adam	January 15th ...	March 5th.
Girdwood, William Prout	November 5th ..	December 3rd.
Gregory, G. M.	March 19th.....	May 7th.
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Hogg, Edward Grindle	April 2nd	May 7th.
Hope, Charles Frederick	March 5th.....	„ „
Holgate, Thomas	November 5th...	December 3rd.
Howard, Edward E.	„ „ ...	„ „
Hughes. T. Vaughan	May 7th	June 4th.
Hurst, George	November 5th ..	December 3rd.
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Hutcheson, John B.	January 15th...	March 5th.
Hunter, Matthew	November 5th ..	December 3rd.
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Newton, Walter	December 3rd...	
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Steel, Robert Elliot	February 19th ..	May 7th.
Stephen, Stephenson	November 5th ..	December 3rd.

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Stocks, J. Marshall	February 5th	March 5th.
Stuart, C. M.	March 5th	May 7th.
Sutton, Francis Napier	December 3rd	
Stoker, Henry.	November 5th	December 3rd.
Tate, John A.	April 2nd	May 7th.
Taylor, Charles Johnson	May 7th	June 4th.
Thomson, Andrew	November 19th	December 17th.
Thorne, Edward E. H.	„ 5th	„ 3rd.
Tyson, Thomas B.	„ „	„ „
Viera, J. Dominie	June 4th	November 19th.
Vulte, Herman, Ph.B.	„ „	„ „
Wallace, Robert	May 7th	June 4th.
Watson, Charles	February 5th	March 5th.
White, Harold	December 4th	February 5th.
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Wormley, T. G.	„ „	„ „
Wrenn, William A.	December 18th	February 5th.
Wright, James C.	June 4th	November 19th.
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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 1. Session 1884–85.

January 15, 1885.—Dr. W. H. Perkin, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. Charles M. Blades, Northwich, Cheshire; Julius B. Cohen, Pendleton, Manchester; Adam Gibson, Leven, Fifeshire, N.B.; John B. Hutcheson, The University, Glasgow; William McD.Mackey, Frodingham, Doncaster; George Patterson, Tufnell Park, London; F. W. Simpson, Mill Hill, Derby; Walter Collingwood Williams, Edgbaston, Birmingham.

The following papers were read :—

1. "On the Atomic Weight of Titanium." By Prof. T. E. Thorpe, F.R.S.

The atomic weight of this element was made the subject of investigation so far back as 1823 by Heinrich Rose. In 1829 Rose published a second series of determinations, which were followed in 1847 by the determinations of Pierre, and in 1849 by those of Demoly. These determinations have given values for Ti varying from 47·92—56·39. In framing his arrangement of the elements in accordance with the Periodic Law, Mendelejeff adopted the number 48 as the atomic weight of titanium. A number less than 50 was in fact demanded by the law. A redetermination of the atomic weight of this element, therefore, was obviously required, not only to fix its value as a chemical constant, but as affording an excellent test of the validity of Mendelejeff's hypothesis.

The exact determination of the atomic weight of titanium is rendered difficult from the circumstance that comparatively few compounds of this element exist which are wholly suitable for the purpose. The author of the present communication has made use of the tetra-

chloride and tetrabromide as the bases of his experiments. He has determined the amounts of chlorine and bromine in these compounds, and also the amounts of titanic oxide which they yield by decomposition with water. He has made in all six series of experiments, based upon the following ratios :—

I	$TiCl_4 : 4Ag$
II	$TiCl_4 : 4AgCl$
III	$TiCl_4 : TiO_2$
IV	$TiBr_4 : 4Ag$
V	$TiBr_4 : 4AgBr$
VI	$TiBr_4 : TiO_2$.

The results are as follows :—

Series I (8 expts.)	48·014
II (5 „)	48·016
III (6 „)	47·969
IV (5 „)	48·031
V (4 „)	48·057
VI (3 „)	47·989

The mean of the whole 31 experiments becomes 48·013, the probable error of the series being $\pm$ 0·021, and the probable error of the result $\pm$ 0·0085.

This value assumes, with Lothar Meyer and Seubert's, that the most probable ratios of Ag, Cl, Br, O, and H are :—

Ag	=	6·7456
Cl	=	2·21586
Br	=	4·99721
O	=	1
H	=	0·06265

In calculating his results, the author has grouped his observations in accordance with the expression—

$$x = \frac{b_1 + b_2 + b_3 + \ldots\ldots + b_n}{a_1 + a_2 + a_3 + \ldots\ldots + a_n} = \frac{[b]}{[a]}$$

Full details of the mode of preparation of the substances made use of, and of the methods of analysis and manipulation, are given in the paper.

The number 48·01 differs but slightly from that obtained by Rose in the experiments on which he set the greatest weight ; it varies, however, by more than two units from the final number adopted by Pierre, viz., 50·25, and which has hitherto been commonly accepted as the most trustworthy value for Ti.

It will be observed, too, that the number 48·01 is in entire accordance with the value required by the Periodic Law; Mendelejeff's prevision thus receives a further experimental confirmation.

Discussion.

Prof. Dewar, referring to the atomic weights adopted by Prof. Thorpe, said that he hesitated whether to accept O = 16 or O = 15·96; in fact, whether or no Marignac's criticism was not after all correct. It was essential, however, that every atomic weight should be determined in a variety of ways—by a variety of methods. With regard to the atomic weights being whole numbers, he felt no longer any doubt, the evidence that there is often a considerable departure being unquestionable, as in the case of magnesium and zinc, and perhaps also of cadmium.

Dr. Gladstone remarked that the fact that there are exceptions does not render it less remarkable that in very many cases the atomic weights are whole numbers.

2. "Note on the Constitution of Propylene-chlorhydrol." By Dr. H. F. Morley and A. J. Green.

It is found that propylene-chlorhydrol, $C_3H_6Cl.OH$, prepared by the action of sulphur chloride on propylene-glycol, yields chloracetone when oxidised either by cold chromic mixture or nitric acid; it therefore consists of the compound $CH_3.CH(OH).CH_2Cl$, with which, perhaps, a small quantity of the isomeride is mixed, as the formation of a small quantity of an aldehyde (possibly chloropropionic aldehyde) was also observed.

3. "The Action of Zinc Ethide on the Benzoate from Propylene-chlorhydrol." By the same.

This reaction was investigated in the anticipation that it would be possible to displace the chlorine by ethyl, the benzoate being used in order to protect the hydroxyl of the chlorhydrol. It is found, however, that chemical change occurs in the manner represented by the equations:—

$$C_6H_5.CO(OC_3H_6Cl) + ZnEt_2 = C_6H_5.CEt\left\{\begin{matrix}OZnEt\\OC_3H_6Cl\end{matrix}\right. = ZnClEt$$
$$+ C_6H_5.CEt\left\{\begin{matrix}O\\O\end{matrix}\right\}C_3H_6.$$

The benzoate and the new product, *ethylphenylketate*, are described. On oxidation, the latter gives benzoic and acetic acids; it is converted

by iodhydric acid into ethylphenylketone and isopropyl iodide; concentrated sulphuric acid has a similar action, the products being the ketone and propylene hydroxide. The authors take occasion to point out that ethylphenylketone is a solid, crystallising in thin plates, which melt at 21°, and not a liquid, as hitherto supposed; it boils at 218° (corr.)

Discussion.

Dr. Armstrong remarked that the action of zinc ethide on the benzoate was, he thought, a normal one, as apparently even in the case of acetic chloride, for example, the oxygen of the carboxyl, and not the chlorine, was first affected. He regretted that the authors had not continued their experiments with the object of settling the question—one of some importance—raised by Markownikoff's and Henry's observations on propylene-chlorhydrol, and that they had not operated with material prepared by the method adopted by these chemists. The comparative study of the chlorhydrol prepared under various conditions, on the one hand, from propylene, and on the other, from its glycol, would probably furnish more valuable information than was to be obtained from the investigation of the ketate described.

Dr. Morley in reply said that the ketate was only prepared after a number of futile attempts to determine the constitution of the chlorhydrol in other ways. He also stated that the yield of chloracetone on oxidation was very unsatisfactory. The glycol used was prepared by distilling glycerol with sodium hydroxide.

4. "On Nitrobenzalmalonic Acids." By C. M. Stuart, M.A.

These acids are prepared by digesting the nitrobenzaldehydes with malonic and acetic acids; that from paranitrobenzaldehyde has already been described to the Society by the author (Trans., 1883, 409).

Orthonitrobenzalmalonic acid crystallises from water in needles melting at 161°, with evolution of carbon dioxide and carbonisation. Analyses of the acid and of its silver and lead salts are given.

Metanitrobenzalmalonic acid melts at 205°, with evolution of carbon dioxide, leaving a residue of metanitrocinnamic acid.

It is noteworthy that whereas benzalmalonic acid and its para- and meta-nitro-derivatives are decomposed on boiling with water, the ortho-acid can be boiled for any length of time with dilute acids without undergoing decomposition.

Ethyl benzylmalonate, cooled by a mixture of ice and chlorhydric acid, is converted by the action of fuming nitric acid into a mixture of the para- and ortho-nitrobenzalmalonate, in which the para-com-

pound preponderates ; this is somewhat remarkable, as ethyl cinnamate yields a larger proportion of the orthonitro-derivative.

5. "Alkaloïds of Nux Vomica. III. Some Experiments with Strychnine." By W. A. Shenstone, Lecturer on Chemistry in Clifton College.

In continuation of his experiments on strychnine, the author has studied the action of bromine upon the alkaloïd, and also the action of nitric acid on bromostrychnine and upon strychnine itself.

Strychnine can be readily and entirely converted into the monobromostrychnine of Laurent by the addition of bromine to a solution of strychnine hydrochloride in about 50 times its weight of water. The properties of monobromostrychnine are given.

The resinous product obtained by Laurent, which is apt to be the chief product obtained by his method, is found to be a dibromide of the above monobromostrychnine ; it has the formula $C_{21}H_{21}BrN_2O_2Br_2$.

By the cautious addition of a solution of bromine in chloroform to a solution of monobromostrychnine in the same liquid, a resinous compound is obtained, which is probably dibromostrychnine.

On treating bromostrychnine and also strychnine itself, with strong nitric acid, besides the nitrostrychnines of various observers, a fair amount of 1 : 2 : 4 : 6 trinitrophenol is produced. This last observation is of importance, as it shows the presence in strychnine of a benzene-ring of carbon-atoms, and probably also of at least one hydroxyl-group, the latter inference being confirmed by the behaviour of strychnine with alkaline oxidising agents.

6. "On the Physiological Action of Brucine and of Bromostrychnine." By Dr. T. Lauder Brunton, F.R.S.

The difference between the effect of brucine and strychnine appears rather to be one of degree than of kind, and to be chiefly dependent on the more ready elimination of brucine. Like strychnine, brucine produces death by convulsions and not by paralysis ; but like curare, it is innocuous when taken into the stomach, though fatal when injected under the skin. Bromostrychnine has an action very much like that of strychnine.

7. "Crystallography of Bromostrychnine." By H. A. Miers, British Museum.

The crystals belong to the rhombic system, and are mostly rectangular tables. Measurements are given.

8. "On the Formation of Pyridine Derivatives." By H. v. Pechman and W. Welsh.

It is pointed out that nothing is as yet known of the character of the changes which occur in plants and which lead to the production of the alkaloïds, and that it has not hitherto been possible to produce alkaloïds by reactions taking place under ordinary conditions of temperature. In coumalinic acid, discovered by one of the authors, and obtained by treatment of malic acid with sulphuric acid (*Ber.*, 1884, 936), however, a body has been discovered which at once reacts with aqueous ammonia even at the ordinary temperature, forming hydroxynicotinic acid,

$$C_5H_3O_2.COOH + NH_3 = OH_2 + C_5H_3N(OH).COOH,$$

an acid which stands in close relation to the alkaloïds. The method of preparing hydroxynicotinic acid and its properties are described, its constitution is fully discussed, and an account is given of its conversion into chloronicotinic and nicotinic acids. Reference is then made to the action of primary amines on ethereal salts of coumalinic acid. Aniline and the methyl salt give the acid methyl salt of *coumalanilidic acid*, $COOH.C_4H_3(NH.Ph).COOMe$, which is converted by boiling with sodium hydroxide solution into sodium phenoxynicotinate, $C_5H_5N(OPh).CO_2Na$, a remarkable change, as it involves the "passage of phenyl from nitrogen to oxygen." The same remarkable isomeric change takes place when the product of the action of methylamine on methyl coumalinate is similarly treated, methoxynicotinic acid being formed.

DONATIONS TO THE LIBRARY.

Denkschriften der kaiserlichen Akademie der Wissenschaften, Wien: Band 47 (1883).

Sitzungsberichte der kaiserlichen Akademie der Wissenschaften, Wien: Bände 88 (1883), 89 (1884): from the Academy.

ALTERATIONS IN THE LIBRARY RULES.

Attention is directed to the fact that Rules 3, 4 and 5 have been amended, and are now as follows:—

3. All Journals of which there are not duplicate copies, and certain books distinguished in the Library copy of the Catalogue by a star, belong to the Reference Library, and are not for general circulation. But Fellows desiring to consult books placed in the Reference Library may make a special application in writing to the Librarian, undertaking to bear all risks of transit, &c., and to return the same within

one month: the Librarian may then at his discretion allow the issue of such books. This regulation does not apply, however, to volumes of Periodicals of which no duplicate copies exist in the Library.

4. The Periodicals placed in the Circulating Library may be issued to Fellows both in volumes and in parts of the current volumes.

5. Books shall be issued either personally to the Fellow desiring the loan, or to a person bringing a written order from him. When a Fellow desires a book or books to be sent to him, he shall send to the Librarian a written order for the same, and shall pay the whole cost of carriage. All books borrowed by Fellows shall be at the risk of the borrower from the moment they are issued or despatched to him.

NOTICE TO AUTHORS OF PAPERS.

To facilitate the preparation of these "Abstracts of Proceedings," all authors are requested to furnish abstracts of their communications, and to send their papers so that they may be in the hands of the Secretaries, if possible, on the Monday before the day of meeting.

Papers read before the Royal Society of London, January 15th, 1885:—

"On the Chemical Composition of the Cartilage occurring in certain Invertebrate Animals." By W. D. Halliburton, M.D., B.Sc.

"On the Constant of Electro-magnetic Rotation of Light in Bisulphide of Carbon." By Lord Rayleigh, F.R.S.

"Absorption-spectra Thermograms." By Captain Abney, F.R.S., and Colonel Festing, R.E.

(It is hoped that it may be possible regularly to publish the titles of papers of special interest to chemists read at the meetings of the various Scientific Societies in the United Kingdom.)

At the next meeting of the Society on Thursday, February 5th, there will be a ballot for Fellows. Professor Frankland, F.R.S., will deliver a lecture "On the Chemical Changes effected by Micro-organisms."

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 2. Session 1884-85.

February 5, 1885.—Dr. W. H. Perkin, F.R.S., President, in the Chair.

Messrs. J. B. Ballard, Frank Broughton, Rev. Dr. Eley, C. C. Hutchinson, Herbert Jackson and C. E. Hutchinson were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Edward Greenhill Amphlett, M.A., Woodside, Clewer, Windsor; Robert Gordon Blaine, B.E., Ridley Road, Forest Gate, E.; Frederick Mark Davies, 3, Glenmohr Terrace, Blackheath; Ernest Howard Farmer, 135, Dulwich Road, S.E.; Charles Watson, 5, Paradise Row, Stockton-on-Tees; Alfred Henry Knight, 321, Upper Parliament Street, Liverpool; Joseph Marshall Stocks, Edenfield, Bury, Lancashire.

The following were elected Fellows of the Society:—Messrs. William Lane Clark, John Norman Collie, Augustus E. Dixon, George Embrey, Arthur George Green, George G. Henderson, George Selkirk Jones, Walter Frederick Parkhurst, Franz Rindskoff, Harold White, Henry B. Whitehead, Alfred C. Wilson, William Albert Wrenn, Alfred C. Young.

A Lecture was then delivered—

9. "On Chemical Changes in their relation to Micro-Organisms." By Professor Frankland, D.C.L., LL.D., F.R.S.

A plant being defined as an organism performing synthetical functions, or one in which these functions are greatly predominant; an animal as an organism performing analytical functions, or one in which these functions greatly predominate: the micro-organisms were classed by the lecturer among animals. Their life essentially depends upon the taking asunder of more or less complex compounds, resolving them into simpler compounds at the expense of potential energy.

As micro-organisms are commonly termed "ferments," and their

analytical operations "fermentations," it is necessary to sharply distinguish between organised ferments and certain bodies which bring about analogous chemical changes, but which are not only not organised, but exist in solution. These latter, or "soluble ferments," as they are commonly termed, are said to act by contact: they produce certain chemical changes in the fermentescible substances without themselves furnishing from their own substance any of the products of change; the effects they produce are essentially analytical, consisting in the assimilation of water and the splitting up of the fermentescible substance into two or more new molecules, and may be brought about by purely chemical means. They differ only, or chiefly, from the organised ferments in that they are unorganised and do not increase in amount during their action upon fermentescible substances, of which a very large, although limited, quantity may undergo transformation by the action of a very minute quantity of the ferment. A list of changes brought about by unorganised ferments was given.

In that portion of the animal kingdom with which we are best acquainted, oxidation is the essential condition of life: it is the kind of action by which the animal changes actual into potential energy. The changes effected by micro-organisms are essentially of the same character as those brought about by the higher orders of animals: that is to say, they are all changes by which potential becomes actual energy. With one or two exceptions, the chemical changes effected by micro-organisms—unlike those produced by soluble ferments—cannot be brought about by other means. The observations of Hatton and others have shown that micro-organisms retain their vitality in presence of a variety of substances which rapidly prove fatal to higher animals; the unexpected fatal effects of spongy iron would seem to promise, however, that there are substances fatal to bacterial life which have no toxic effect on more highly organised animals. It has not yet been shown that any degree of cold, however intense, is fatal; animation may be suspended, but it is restored when the temperature rises. With regard to heat, the lowest fatal temperature recorded is 40° C., but many species can withstand much higher temperatures. Chloroform and compressed air are said to arrest their action, but to have no influence in preventing the changes brought about by unorganised ferments. The position of micro-organisms in nature is only just beginning to be appreciated; their study both from chemical and biological points of view is, however, of the highest importance to the welfare of mankind, and leads the inquirer right into those functions of life which are still shrouded in obscurity.

In the course of the lecture the best known micro-organisms and the chemical reactions due to them were passed in brief review.

Prof. Frankland also referred to the following results of an experiment made in the month of June, in which fresh urine was allowed to stand for 25 days in a clean glass vessel.

	Residue left on evaporation and drying at 100° C.	Organic carbon.	Nitrogen as urea and other organic matter.	Ammonia.	Microscopical observations.
Fresh urine	4817·0	943·81	1080·27	142·40	No bacilli.
„ „ after 1 day..	—	940·46	1095·05	136·65	„
„ „ „ 3 days.	—	928·76	1106·70	136·50	„
„ „ „ 5 „ .	—	882·66	983·26	288·55	Sparse bacilli.
„ „ „ 7 „ .	—	739·82	900·80	338·60	
„ „ „ 9 „ .	—	682·99	784·93	485·12	Numerous bacilli.
„ „ „ 11 „ .	—	621·02	744·64	534·80	Very numerous bacilli.
„ „ „ 14 „ .	—	559·22	481·49	870·62	Vast numbers of bacilli.
„ „ „ 16 „ .	—	530·68	492·04	881·87	Mostly still.
„ „ „ 18 „ .	—	487·01	355·25	990·78	„ „
„ „ „ 21 „ .	—	466·43	278·22	1105·75	All dead or still.
„ „ „ 23 „ .	—	451·43	347·45	1017·25	„ „
„ „ „ 25 „ .	2718·0	460·78	283·90	1070·50	
After allowing for evaporation	2045·5	346·77	213·66	805·63	

The results of these observations and determinations which were made during the month of June show conclusively that, previously to the development of *Bacillus ureæ*, the chemical composition of the urine remained practically unchanged; but with the appearance of micro-organisms, a diminution of organic carbon and a transference of nitrogen from the organic to the ammonia column immediately began. As regards rapidity, this change marched *pari passu* with the density of population, and reached its maximum about the 12th day; for during the three days (11th to 14th) nearly 10 per cent. of carbon disappeared, whilst more than 85 per cent. of the organic nitrogen became ammonia. After the 14th day the rate of change became much slower, on the 18th day the bacilli were mostly either dead or motionless, whilst on and after the 23rd day no more moving bacilli were seen. Altogether the quantity of carbon converted into carbonic anhydride, after allowing for concentration of the liquid by evaporation, amounted to 597·04 parts per 100,000 of liquid, or 63·3 per cent. of the total quantity; whilst the quantity of organic nitrogen converted into ammonia was 546·19 parts per 100,000, or 50·6 per cent. of the whole. These proportions show that all the organic nitrogen contained in the urea was not converted into ammonia. It no doubt escaped as free nitrogen, in accordance with Frank Hatton's observation.

In the original urine the proportion of organic carbon to organic nitrogen was as 1 : 1·15, whilst, after the action of the bacilli, it was as 1 : 0·62.

Prof. Burdon Sanderson said that the main difficulty met with in studying the effects of micro-organisms arose from the fact that it was always difficult and often impossible to distinguish between different organisms. Chemists might naturally turn to biologists for aid in the matter, but biologists must admit the existence of this difficulty. We are fully acquainted with the life history of only one pathogenic organism—the *Anthrax bacillus;* of this, thanks to Koch, we know, however, a great deal. The method followed by biologists in studying pathogenic forms was, in the first instance, to prepare a pure cultivation of the organism, and then to obtain the proof that the organism produces its proper effect when transferred to a living animal. The morphological relations of bacteria with plants could not be questioned, but he thought it was really of little consequence for practical purposes whether ferment organisms were regarded as animals or plants; what we want to know is, what are the conditions under which an organism is produced, and its life history. He was in the habit of calling them microphytes, as being a neutral term.

Prof. Ray Lankester was astonished at the definite way in which Prof. Frankland had classed the ferment organisms with animals. Naturalists were led to regard them as plants from examining their relations to other organisms. He agreed with Prof. Sanderson that "microphyte" was a good name for them, although not precisely for the same reason, but because it really meant a little plant. He stated that it was held hitherto that a micrococcus induced the ammonic change in urine, and not a bacillus as figured by the lecturer. For the purpose of chemical investigation, it was essential to have a pure cultivation. It was curious that the nitrifying organism had not been isolated; its presence had only been inferred, and it had never been satisfactorily separated and identified, although inconclusive statements and observations purporting to inform us as to the form of that organism had been published.

Dr. Brunton said that it was highly probable that the symptoms occurring in certain diseases were due to poisons formed by the action of organisms and not directly to the organisms themselves. This was not improbably the case in cholera. Micro-organisms may even produce substances fatal to themselves, *e.g.*, phenyl compounds. This is also the case with higher organisms, the retention of the urine in man being often attended with fatal results. Although cholera was very probably due to the presence of low organisms, the symptoms were so very like those produced by certain poisons, that it was very difficult

to diagnose cases of poisoning by arsenic from cholera cases. The cholera poison was probably of an alkaloïdal character and related to the ptomaïnes. Pepsin converted albuminoïds into peptones, but it was important to note that Brieger had observed that sometimes an alkaloïd having an action similar to curare was formed during peptic digestion, and an alkaloïd having a similar action had been obtained from human urine. These facts rendered it probable that alkaloïds might be formed in the intestinal canal and absorbed into the general circulation.

Prof. M. Foster said that the question whether the micro-organisms in question were plants or animals was to him a matter of indifference compared to the question—what was the exact nature of the action by which the organism effected the chemical change? He desired to point out that in certain cases, as in the ammonic conversion of urea, the same change, in this case the conversion of urea into ammonium carbonate, was effected, on the one hand, by a micro-organism, a micrococcus or bacillus, and on the other hand by an unorganised ferment. His friend Mr. Sheridan Lea informed him that he had evidence of both these causes of ammonic conversion of urea. Now, was the action in both cases the same? The idea had naturally occurred that the organism produced its effect by producing an organised ferment. But all attempts to prove the production of such a secretion, so to speak, of a ferment had failed. If such a ferment were produced, it was destroyed or disappeared during its action, whereas ordinary unorganised ferments such as pepsin, &c., were not destroyed at all during their activity, or were destroyed very slowly. On the whole, the probability was that the micro-organism and the unorganised ferment produced the same result in different ways; ought not that *difference* to offer the key for solving the problem?

He further desired to remind the Fellows that actions similar to those of these micro-organisms were continually being carried on by the constituent elements of man and other macro-organisms, and would wish, in illustration, to call their attention to the act of secretion by a secreting cell, such as the pancreatic cell. We had evidence that certain constituents of pancreatic juice existed in the cell, not in the form in which they appear in the juice itself, but in an anterior more complex condition. Thus trypsin occurs in the pancreatic cell not as trypsin but as trypsinogen. Now this trypsinogen, and also probably other "mothers" of the constituent of the juice, exist in the protoplasm of the cell as *discrete granules, lodged in the meshes of the protoplasm, separated from the protoplasm by films of fluid.* Yet the protoplasm, stirred by some nervous impulse, is able to produce a change in these granules, so that they are discharged to form the

secretion. How does the protoplasm work upon these granules? Does it discharge something into the fluid of its meshes, which something acts upon the granule, or does it work upon the granule through the film of fluid surrounding the granule, by something which is a sort of "action at a distance." The action then in this case is very comparable to the action of the micro-organisms in question. It is for the chemists to throw light on the exact nature of the changes produced, and when this is done, we may hope to learn how the change is brought about, but not until this is done.

Mr. Thiselton Dyer said that from the botanist's point of view he was struck with the universality of fermentative changes. Though they were so predominant a feature in the life of the lower plants, this was only an extreme manifestation of what, perhaps, all plants were capable of, if the conditions demanded it Thus Pasteur, following up an experiment of Bérard's, found that a rhubarb leaf in an atmosphere of carbon dioxide yielded after 48 hours, though apparently unchanged, small quantities of alcohol. The breaking up of molecules of large thermic equivalent into those of less, supplies the energy needed for the continued life of the tissues, and is the *raison d'être* of the process.

But plants also set up fermentative changes external to themselves, as it were incidentally and without any obvious benefit. The investigation of Beyerinck on the production of gum by plants yielded most remarkable results. It is due to a disease which is highly contagious, and which is caused by a fungus (*Coryneum*). This produces a ferment which changes the cell-walls into gum. But what is most remarkable is that even after the disappearance of the fungus which initiated the changes, the cells of the host plant take on a morbid habit of growth, and themselves continue the production of the ferment and therefore of gum to their own hurt. The problem is here of the most complicated kind.

The series is ended by cases such as that of *Withania coagulans* (and many others are now known), where plants throw off, as bye-products of their metabolism, ferments as effective as rennet, without deriving any perceptible advantage from their possession. That plants use in working up their reserve-proteïds proteolytic ferments just as animals do, cannot be doubted. But even these they occasionally, as in the Papaw, produce in utter disproportion to their own possible requirements.

Mr. Warington said with regard to the difference between animals and plants, he thought the fact had been somewhat overlooked that plants are able to obtain their nitrogen from such simple compounds as ammonia and nitrates, whereas animals appear to require to have the nitrogen presented to them in an albuminoïd form.

As to the nature of the nitrifying organism, Müntz and Schlösing

claim to have isolated it and have described it. A friend who had microscopically examined his purest cultivations at Rothamsted, had been unable to find bacilli, but they appeared to contain a micrococcus. [Prof. LANKESTER, interposing, remarked that the growth sent to him by Mr. Warington consisted of bacilli, and nothing else.] In explanation, Mr. Warington said that in one of his earlier papers he had mentioned that white films appeared on some of his solutions. Prof. Lankester had examined these, but he had since found that the bacilli of which they consisted were incapable of nitrifying ammonia. Latterly he had followed Dr. Klein's method, and had introduced the infecting matter into the sterilised cultivation liquid by means of a capillary pipette, which was pushed through the cotton-wool plug closing the tube or flask; since he had done this, the films referred to had never been formed.

Dr. THUDICHUM agreed that the ammonic change was produced in urea by a micrococcus. The study of microphytes and of the chemical changes produced by them in the human body and in the bodies of animals was of the greatest importance. He questioned whether their action was always so specific, however, as was commonly supposed. He would also call attention to the fact that one micro-organism will kill another: thus, after plastering wine, in consequence of the removal of the tartrate, the microphyte which produces ropiness is crowded out by alcoholic forms.

Dr. STEVENSON called attention to the importance of obtaining more information as to the alkaloïdal bodies formed by the action of micro-organisms.

Prof. FRANKLAND replied that he did not mean absolutely to say that in his experiments the work was done by the *Bacillus ureæ*, but the diagram was a faithful representation of what he saw; he attributed the action to the particular organism, because it commenced when the organism appeared, and ceased when the bacilli became motionless. The necessity of studying the actions of pathogenic organisms had been prominently brought forward in the discussion. He thought there was a substantial difference between the class of chemical changes effected by plants on the one hand and by animals on the other; animals more particularly consumed as food those compounds in which much energy was stored up.

ADDITIONS TO THE LIBRARY.

I. Donations.

Chemical News. Vols. 15 and 16: from Sir H. E. Roscoe.

Photographic News: from Dr. Atkinson.

Nova Acta Academiæ Cæsareæ Leopoldino-Carolinæ Germanicæ Naturæ Curiosorum. Vols. 45 and 45: from the Academy.

Year Book of Pharmacy and Transactions of the British Pharmaceutical Conference, 1884: from the Conference.

Calendar of the Pharmaceutical Society, 1885: from the Society.

Salpetersäure-Goldnitrat und einige neue Derivate desselben, von P. Schottlander: from the Author (*Pamphlet*).

By Purchase.

Chemie der Kohlenstoffverbindungen: V. v. Richter. 4te Auflage, 1885.

Pyrochemische Untersuchungen: C. Langer and V. Meyer. 1885.

Das Sauerstoff-Bedürfniss des Organismus: P. Ehrlich. 1885.

La Pile électrique: A. Niandet. 1885.

Chimie appliquée à l'Art de l'Ingéneur: C. Leon Durand-Claye. 1885.

Titles of Papers of interest to Chemists recently read before Societies in the United Kingdom:—

(*a*.) "On the Origin of the Proteids of the Chyle and the Transference of Food Materials from the Intestine into the Lacteals." By E. A. Schäfer, F.R.S.

(*b*.) "Observations on the Chromatology of Actiniæ." By C. A. MacMunn, M.A., M.D.

(*c*.) "The Relation of Bacteria to Asiatic Cholera." By E. Klein, M.D., F.R.S. Royal Society of London: (*a* and *b*) January 22nd; (*c*) February 5th.

"On Condensation and Evaporation." By Prof. Tait. Royal Society of Edinburgh, February 2nd.

"Final Report bearing upon the Question of the Condition in which Carbon exists in Steel." By Sir Frederick Abel, C.B., D.C.L., F.R.S. Annual General Meeting of the Institution of Mechanical Engineers, January 30th.

"Note on Selenocarbamide or Selenium-urea;" and "Note on Schiff's Method for the Distinction of Aldehydes from Ketones." By Prof. Emerson Reynolds. Royal Dublin Society, January 19th.

At the next meeting of the Society on Thursday, February 19th, the following papers will be read:—

"On Ethylic Benzoylacetate and some of its Derivatives." Part II. By Dr. W. H. Perkin, Junr.

"On Toughened Filter Papers." By E. E. H. Francis.

"The Detection and Estimation of Iodine." By Ernest H. Cook.

"Note on Methylene Chlor-iodide." By Prof. J. Sakurai.

"A Quick Method for the Estimation of Phosphoric Acid in Fertilisers." By J. S. Wells.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 3. Session 1884-85.

February 19, 1885.—Dr. W. H. Perkin, F.R.S., President, in the Chair.

Messrs. G. S. Bowler, T. R. Duggan, A. G. Green, W. W. J. Nicol, W. F. Pankhurst, T. A. Rickard, F. Rindskoff, P. C. Thomas and H. H. Whitehead, were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. George Harrison Genmell, 13, Peel Street, Liverpool; William Benjamin Hards, St. John's College, Battersea; Thompson Muskett, Walton Lane, Stanley Park, Liverpool; and Robert Elliot Steel, Spring Cliffe House, Heaton Road, Bradford.

The President declared that the following changes in the Council were recommended to the Society:—

As President: Dr. Hugo Müller, F.R.S., vice Dr. Perkin, F.R.S.

As Vice-Presidents: Mr. W. Crookes, F.R.S. and Prof. W. A. Tilden, F.R.S., vice Dr. Voelcker (deceased) and Dr. Griess, F.R.S.

As Foreign Secretary: Dr. F. R. Japp, vice Dr. Hugo Müller.

As Ordinary Members of Council: Prof. F. Clowes, Mr. A. E. Fletcher, Prof. G. C. Foster, F.R.S. and Mr. Ludwig Mond, vice Dr. Japp, Dr. Hodgkinson, Mr. D. Howard and Prof. Schorlemmer.

Mr. R. H. Davis, Dr. P. F. Frankland and Mr. Makins were appointed to audit the Treasurer's accounts.

The President announced that Mr. Warren de la Rue, F.R.S., had presented a bust of the late Prof. Dumas.

The following papers were read:—

10. "On Benzoylacetic Acid and some of its Derivatives." Part II. By Dr. W. H. Perkin, Jun.

Referring to Part I of his research, the author states that the substituted benzoylacetates may be purified by distillation under reduced pressure. *Ethylic ethylbenzoylacetate* and *allylbenzoylacetate*, as thus purified, are described. An account of further experiments on the hydrolysis of these bodies is given: it was not found to be possible to prepare the corresponding acids from them in a pure state, benzoic acid being also produced, in some cases in very considerable proportions, even if only dilute alcoholic potash solution were used; more encouraging results were obtained with the ethyl-derivative on using concentrated sulphuric acid as hydrolytic agent, and a quantity of pure benzoylacetic acid was prepared from ethylic benzoylacetate by means of this reagent.

Ethylic benzoylisonitrosoacetate, $C_6H_5.CO.C(N.OH).COOEt$ (? *benzoylhydroximodoacetate*), prepared from nitrous acid and ethylic benzoylacetate, crystallises in long colourless needles melting at 120—121°; it easily dissolves in alkalis, forming a yellow solution; it decomposes when distilled, becoming carbonised, and hydrogen cyanide is produced. Contrary to expectation, when submitted to the action of a dilute aqueous solution of potassium hydroxide, it does not furnish isonitrosoacetophenone, but instead a crystalline body, which apparently has the formula $C_9H_8O_4$, is produced.

Ethylic dibenzoylacetate, $CH(CO.C_6H_5)_2.COOEt$, is formed by consecutive treatment of the benzoylacetate with sodium ethoxide and benzoyl chloride. Dibenzoylacetic acid prepared from it by treatment with alcoholic potash, &c., melts at 109°; when rapidly heated in small quantities, a part distils unchanged, but the greater part is resolved into carbon dioxide and *Dibenzoylmethane*. Its aqueous solution is coloured a dirty red by ferric chloride. It slowly dissolves in solutions of ammonia, sodium hydroxide and sodium carbonate; several of its salts are described. It is converted by boiling with dilute sulphuric acid into methylphenylketone, benzoic acid and carbon dioxide. Experiments made with the object of converting ethylic dibenzoylacetate into the tribenzoylacetate by consecutive treatment with sodium ethoxide and benzoyl chloride appear to indicate that such a body may be formed in this manner.

Dibenzoylmethane crystallises from alcohol in flat rhombic plates, measurements of which are given. It melts at 81°; it is easily soluble in alkalis. By consecutive treatment with sodium ethoxide and benzoyl chloride, it is converted into *Tribenzoylmethane*, $CH(CO.C_6H_5)_3$. This latter compound crystallises from hot alcohol in almost microscopic needles, melting at 224—225°; it is easily soluble in an alcoholic solution of potassium hydroxide.

Phenyllactic acid, $C_6H_5.CH(OH).CH_2.COOH$, obtained by reducing ethylic benzoylacetate with sodium amalgam, &c., crystallises from

benzene in aggregates consisting of fine needles melting at 93—94°; a crystalline body of the empirical formula C_5H_4O is produced together with it.

It is remarkable that on submitting ethylic benzoylacetate to the action of phosphorus pentachloride, a chlorocinnamic acid of the formula $C_6H_5.CH.CCl.COOH$ is produced; the reaction therefore is one involving isomeric change.

If a mixture of ethylic benzoylacetate and benzaldehyde cooled to 0° be saturated with hydrogen chloride, a reaction gradually takes place similar to that observed by Claissen in the case of ethylic acetoacetate, *ethylic benzalbenzoylacetate*, $C(CH.C_6H_5)(CO.C_6H_5).COOEt$, being formed. This body crystallises from ether in large monoclinic prisms, measurements of which are given; it melts at 98°. Attempts to hydrolyse it with muriatic acid and with alcoholic potash gave negative results.

11. "On Toughened Filter-paper." By E. E. H. Francis.

Filter-paper which has been immersed in nitric acid, rel. den. 1·42, and washed with water, is remarkably toughened, the product being pervious to liquids and quite different from parchment paper made with sulphuric acid. Such paper can be washed and rubbed without damage, like a piece of linen. The paper contracts in size under the treatment and the ash is diminished; it undergoes a slight decrease in weight and contains no nitrogen. Whereas a loop formed from a strip 25 mm. wide of ordinary Swedish paper gave way when weighted with 100—150 grams, a similar loop of toughened paper bore a weight of about 1·5 kilo. The toughened paper can be used with the vacuum pump, in ordinary funnels without extra support, and fits sufficiently closely to prevent undue access of air, which is not the case with parchment paper. An admirable way of preparing filters for the pump is to dip only the apex of the folded paper into nitric acid and then wash with water; the weak part is thus effectually toughened.

12. "The Detection and Estimation of Iodine." By Ernest H. Cook, B.Sc. (Lond.).

The usual tests for iodine when existing as an iodide are rendered somewhat difficult by the circumstances that nitrous acid liberates bromine as well as iodine, while if an excess of chlorine be employed, colourless chlorides of bromine and iodine are formed. These difficulties become of importance when it is desired to detect small quantities of iodides in the presence of comparatively large quantities of bromides, or when a quantitative estimation is to be made of the iodine.

To avoid these difficulties, the author proposes to use hydrogen peroxide, which is added to an acetic acid solution. Under these circumstances, the whole of the iodine is separated from the iodide, while bromides and chlorides are unaffected.

Details of the methods of employing the test for qualitative and quantitative purposes are given; in the latter case, the iodine is extracted by means of $CHCl_3$, the solution is washed with a little water to remove hydrogen peroxide, and the titration of the iodine then performed in the usual manner.

Discussion.

Mr. Groves said that he had very successfully used nitrous acid in determining small quantities of iodine in presence of much chlorine.

Dr. Japp did not know that the method described was better than the old well-known process of adding titrated chlorine water in presence of carbon bisulphide until the colour of the iodine disappeared, which took place when 5 atomic proportions of chlorine to 1 of iodine had been added.

Mr. Groves had found this latter a far less convenient process.

Dr. Stevenson spoke to the same effect, and said that he also had found the nitrous acid method satisfactory.

13. "Note on Methylene Chlor-iodide." By Prof. J. Sakurai.

This compound was obtained by heating methylene iodide with iodine chloride; it is a colourless oil, which boils at 109—109·5°, of relative density (referred to water at the same temperature) 2·447 at 11° and 2·444 at 14·5°. It is identical with the substance previously obtained by the author from mercuric methylene chloriodide and iodine (Trans. 1882, p. 360), and it is therefore concluded that this mercuric compound has the formula $CH_2Cl.HgI$.

14. "A Quick Method for the Estimation of Phosphoric Acid in Fertilisers." By J. S. Wells, Columbia College.

Finding the ammonium molybdate method too long and tedious when many analyses of fertilisers had to be done, the author has adapted Joule's citric acid method as a gravimetric process. He employs two solutions: A, consisting of citric acid 900 grams, ammonia solution (rel. den. 0·92) 1400 c.c., water 500 c.c.; and B, a strong solution of magnesium citrate. 1 gram of the fertiliser is fused with sodium carbonate and nitrate, dissolved in nitric acid, and the silica filtered off. To the filtrate some of solution A is added, and the whole allowed to stand for half an hour; enough of solution B is then added to precipitate the phosphoric acid. For the author's

experiments, a test solution was made up of sodium phosphate, calcium chloride and ammonia-iron alum, so as to contain P_2O_5, 19·83 per cent., CaO, 25 per cent., Fe_2O_3, 3 per cent.; equal portions were taken for analysis, the comparison of his results with theory being given in a table. He compares his own method with the ammonium molybdate method on several fertilisers with the following results:—

	Ammonium citrate method.	Ammonium molybdate method.
1.	4·23 per cent.	4·23 per cent.
2.	18·36 ,,	18·18 ,,
3.	3·42 ,,	3·64 ,,
4.	14·01 ,,	13·92 ,,

Discussion.

Mr. Riley did not think the method described a simple one. He stated that he had been working on a process which he hoped would enable him to easily determine phosphoric acid in a substance like basic iron cinder, which contained about 19 per cent. The cinder is dissolved in nitric acid and taken up with alcohol, the alcohol being then evaporated off, and the phosphoric acid titrated with uranium nitrate. He had not yet been altogether successful, however.

Mr. F. J. Lloyd said that the accuracy of the results would depend on and would vary with the kind of material examined. A very similar method had already been published, the essential feature in it being that the lime was not taken out; after making many experiments on this method for Dr. Voelcker, he was led to conclude that it was not possible to obtain accurate results with different substances.

15. "On the Luminosity of Methane." By Lewis T. Wright, Assoc. M.I.C.E.

Pure methane was prepared by Gladstone and Tribe's method by the action of the copper-zinc couple on methyl iodide. The gas was obtained free from methyl iodide vapour by passing it through tubes fixed in a horizontal position and packed with copper-zinc, which was kept moistened with alcohol, the alcohol vapour being removed by scrubbing with sulphuric acid. It was burned in a London Argand burner, the chimney of which was fitted with a cap for the purpose of limiting the air supply to the quantity most favourable to the development of luminosity. The methane flame was compared with a Methven Standard burner supplied with 18-candle gas, *i.e.*, with a light equal to two sperm Parliamentary candles.

The results obtained were—

Rate of consumption per hour corrected to 60° F. and 30″ B. cub. ft.	Candles observed.	Candles per 5 cub. ft. per hour calculated.
2·78	2·9	5·20
4·46	4·6	5·15

The author proposes to extend his observations to ethane and propane.

Discussion.

Mr. Lloyd doubted the accuracy of the Methven Standard.

Dr. P. F. Frankland asked whether the author had analysed the gas; the results obtained appeared to him to be too high. He had found that the methyl iodide was not all removed even after bubbling the gas through fifteen bulbs containing antimony pentachloride. The method adopted for developing the maximum illuminating power of the methane was extremely interesting.

Dr. Armstrong thought that the method of removing methyl iodide adopted by the author was more likely to be successful than that described by Dr. Frankland: it was well known that air laden with sulphuric anhydride could be bubbled through a very long column of water without the removal of the anhydride being effected.

16. "On the Oxides of Nitrogen." By Prof. W. Ramsay and J. Tudor Cundall.

In this research it is shown—

1. That the green or blue liquid obtained by the action of arsenious anhydride on nitric acid consists of a mixture of nitrous anhydride and nitric peroxide, in proportions depending on the strength of the nitric acid and the temperature at which the volatile liquid is condensed.

2. That if a dehydrating agent, such as sulphuric acid, be present in sufficient quantity the distillate consists of pure peroxide, and that this process is by far the most convenient one for the preparation of the peroxide.

3. That if oxygen be passed over the blue liquid, the vapours condensed in a freezing mixture are still blue or green; a great excess of oxygen is necessary to effect conversion from nitrous anhydride into peroxide.

4. That when excess of nitric oxide is passed along with the peroxide into a cooled bulb, the trioxide is produced, the amount of trioxide depending on the temperature of the condenser.

5. The vapour-density of a liquid of a deep blue colour, containing about 30 per cent. of trioxide and 70 per cent. of peroxide, shows that the trioxide cannot exist in the gaseous state, but at once dissociates into nitric oxide and peroxide on changing to gas. The theoretical

vapour-density of such a mixture was calculated from a formula deduced from the second law of Thermodynamics by I. Willard Gibbs, which shows the relations between temperature, pressure and vapour-density of the mixture of NO_2 and N_2O_4 in the gaseous peroxide; and it was found that the vapour-densities of a mixture of $(NO_2 + N_2O_4)$ (partly present in the original liquid as peroxide, partly formed by the decomposition of the N_2O_3 present into NO and $(NO_2 + N_2O_4)$) with the NO produced by the decomposition of the N_2O_3, calculated by means of Gibbs' formula, are identical, within limits of experimental error, with those obtained by direct experiment.

6. The presence or absence of moisture does not appear to affect the reaction between NO and O_2.

7. It is probable that N_2O_3 undergoes dissociation with rise of temperature, even while liquid.

Discussion.

Dr. Armstrong said that he had listened to the paper with great interest, as he had made numerous experiments on the subject, and had long been of opinion that N_2O_3 did not exist, at all events as gas. The authors' observations, whereby they were led to this conclusion, were of considerable importance, and it was to be hoped that ere long confirmatory evidence that would more directly appeal to chemists would be forthcoming. It was noteworthy that there was no recorded evidence proving the existence of N_2O_3 as gas. Gay-Lussac's experiments, published in 1816, showed that nitric oxide and oxygen only reacted in the proportions to form N_2O_4, and that reaction in proportions corresponding with the production of N_2O_3 only took place in presence of alkali.

The method adopted by the authors did not suffice to prove the existence of N_2O_3, even as liquid, and their results could be equally well interpreted on the assumption that they were dealing with a solution of NO in N_2O_4. It was to be expected that N_2O_4 would be a good solvent of NO, as it appeared to be the rule that bodies which are related are easily miscible, phosphorus, for example, being very soluble in PCl_3, and sulphur in CS_2 and S_2Cl_2. One observation made by the authors did, however, support their view, viz., the observation that the blue liquid was with great difficulty oxidised by passing oxygen into it.

In all his experiments, Dr. Armstrong had found that the reactions attributed to N_2O_3 could be equally well effected by a mixture of N_2O_4 and NO. As to the action of arsenious oxide on nitric acid, in his opinion, *nitrous acid* was *the* product, and the manner in which this underwent change entirely depended on the conditions. In dilute solution, NO would be produced in accordance with the equation:

$3HNO_2 = 2NO + HNO_3 + H_2O$; but in presence of nitric acid the reaction $HNO_2 + HNO_3 = N_2O_4 + H_2O$ would take place, and would more and more preponderate the less the amount of water present. The addition of sulphuric acid would of necessity favour the latter mode of change. When N_2O_4 is passed into sulphuric acid, nitrosyl sulphate and nitric acid are formed; in presence of NO, the latter is reduced to nitrous acid which also forms nitrosyl sulphate with the sulphuric acid, so that a mixture of NO and N_2O_4 in proper proportions precisely acts as though it were N_2O_3.

Mr. Groves said that in preparing nitrosyl sulphate he had found that very little was formed when very concentrated nitric acid and arsenious oxide were used to produce the nitrous gas; and that it was difficult to reduce the solution of HNO_3 in H_2SO_4 by NO.

Dr. Wright mentioned that he recollected the late Mr. Chapman telling him that he had come to the conclusion that N_2O_3 did not exist as gas, but he did not know what experiments he had made on the subject.

Prof. Ramsay, in reply, said that he thought the production of a blue liquid on passing a colourless gas into a brown liquid was good evidence of the production of a distinct compound. (Peligot's experiments render it highly probable that the blue colour results from the introduction of traces of water.—H. E. A.) Numerous cases could be cited of the non-existence of compounds as gas which were well known as liquids or solids—chloral-hydrate for example.

ADDITIONS TO THE LIBRARY.

Donations.

The Chemist. Vols. 1–7, 1840–1846: from Mr. Watson.

Geology of Cornwall: by Brenton Symons: from the Author.

Paper read before the Royal Society of London, February 12:—

"Note on the Condensation of Gases at the Surface of Glass." By J. T. Bottomley, M.A., F.R.S.E.

At the next meeting of the Society on Thursday, March 5, there will be a ballot for Fellows.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 4. Session 1884-85.

March 5th, 1885.—Dr. W. H. Perkin, F.R.S., President, in the Chair.

Mr. William Lane Clarke was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Frank Harris Alcock, Golden Hill, Stoke-upon-Trent; Matthew Cannon, Lavender Hill, S.W.; Martin Dechan, Hawick, N.B.; Charles Frederick Hope, Field View House, Grosvenor Terrace, York; N. H. J. Miller, Ph.D., 8, Oppidans Road, N.W.; Alexander Milne, Bombay; C. M. Stuart, M.A., High School, Newcastle, Staffordshire; William Palmer Wynne, B.Sc., 5, Honeywood Road, Harlesden, N.W.

The following were elected Fellows of the Society:—

Messrs. E. G. Amphlett, C. M. Blades, R. G. Blaine, Julius B. Cohen, F. M. Davies, E. H. Farmer, Adam Gibson, John B. Hutcheson, A. H. Knight, William Mc D. Mackey, George Patterson, F. W. Simpson, Joseph M. Stocks, Charles Watson and Walter C. Williams.

The following papers were read:—

17. "On the Conversion of Pelouze's Nitrosulphates into Hyponitrites and Sulphites." By Prof. E. Divers, M.D. and Tamemasa Haga.

The nitrosulphates may be regarded as thiosulphates in which nitric oxide takes the place of sulphur; in accordance with this view, the authors find that just as thiosulphates are converted by treatment with sodium into sulphite and sulphide, so nitrosulphates become sulphite and hyponitrite; they represent the change by the equation: $(SO_3K)(N_2O_2)K + 2Na = (SO_3K)Na + Na(N_2O_2)K$, and propose to substitute the term *nitrososulphate* for nitrosulphate. The experi-

ment was performed by digesting potassium nitrososulphate dissolved in a concentrated solution of potassium hydroxide with sodium amalgam.

Discussion.

Prof. Odling looked upon the disruptive hydrogenation of the nitrosulphates effected by the authors as a reaction of considerable interest from its associating these salts with the thiosulphates in their mode of decomposition not less than in their mode of formation. He was disposed to think, however, that the view itself put forward by the authors was the prevailing view as to the constitution of the nitrosulphates. With regard to the nature of the class of hyponitrites discovered some time back by Dr. Divers, he would suggest the possibility, at any rate, of these salts being metallic derivatives of an unstable nitramide, $NH_2.NO_2$, a body resulting from the abstraction of one unit of water for each unit of ammonia in nitrate of ammonia, the nitrile, or nitrous oxide, resulting from the abstraction of two units of water for each unit of ammonia. This suggestion as to the hyponitrites would not necessarily affect the view put forward with respect to the nitrosulphates, but would allow of their being also regarded as sulphonate-derivatives, $(KSO_3)NK.NO_2$, of the hypothetical nitramide. (In his second paper Dr. Divers himself suggests these formulæ.)

Dr. Japp thereupon pointed out that the amides as a rule take up water, whereas hyponitrous acid very readily splits up into water and nitrous oxide. The property of readily forming anhydrides is peculiar to dibasic acids; now Zorn's experiments went far to prove that hyponitrous acid was dibasic, so that the formula HO.N.N.OH was to be preferred.

18. "On the Constitution of some Non-Saturated Oxygenous Salts and the Reaction of Phosphorus Oxychloride with Sulphites and Nitrites." By Prof. E. Divers, M.D.

The object of the paper is to show that non-saturated oxygenous metallic salts differ from those which are saturated, not in the manner in which they are universally represented as doing, viz., in having their negative elements of lower than maximum valency, but in being less "oxylic" than the saturated salts of the same element, or in the case of salts of mon-acids not oxylic at all. Thus the author maintains that the sulphites are to be represented by formulæ such as $Ag(AgO)SO_2$, and not $(AgO)_2SO$; the nitrites by formulæ such as $AgNO_2$, not AgO.NO.

The current belief that the sulphites are dioxylic appears to rest on

the fact that they are less stable than the sulphates; and on the conviction that all oxygenous salts, including sulphites, are oxylic, a conclusion which has been deduced from experiments on the action of PCl_5 and $POCl_3$. The author argues, however, that the thionyl chloride, $SOCl_2$, obtained on treating a sulphite with PCl_5, results from some secondary change. Assuming sodium sulphite to be $NaSO_2.ONa$, the transition product $NaSO_2Cl$ would be formed; this would decompose into NaCl and SO_2, and the SO_2 would react upon PCl_5, forming $SOCl_2$. It is shown that no $SOCl_2$ results from the action of $POCl_3$ on either calcium, or lead, or sodium sulphite, and therefore the argument based on the assumed production of $SOCl_2$ by means of this reagent falls to the ground. The production of chloride and phosphate together with SO_2 appears indeed to afford direct evidence of the "sulphonic" constitution of the sulphites, as the reaction appears to be $3NaSO_2.ONa + POCl_3 = 3NaCl + (NaO)_3PO + 3SO_2$.

As evidence that the sulphites are not dioxylic, the following reactions are discussed by the author:—1. The action of heat upon sulphites, whereby thiosulphate is produced (Geuther); taking into consideration the conclusive evidence there is that in thiosulphates half the sulphur occupies the place of half the oxylic oxygen in sulphates, the formation of a thiosulphate affords an unmistakeable indication that in the sulphites the metallic radicle is partly in direct union with the sulphur, as if both metal and sulphur were oxidised no mode of reaction is open by which a sulphide could be formed. The author quotes experiments showing that the production of thiosulphate is due to the reduction of sulphur dioxide to sulphur by the sulphite. 2. On addition of SO_2, or of a sulphite, to a solution of quinine in sulphuric acid, the fluorescence is destroyed. This is of importance as proving the partly non-oxylic nature of sulphurous acid, since Stokes has shown that a haloïd or non-oxylic acid quenches the fluorescence of an oxylic salt of quinine. 3. Mixed sulphites of silver are readily obtained, even silver chloride being freely soluble in solutions of sulphites of alkali-metals. It is well known that silver does not enter into the composition of mixed salts of acids which are exclusively oxylic, but that such salts are readily enough prepared from the haloïd acids. 4. Spring's observations on the formation of sulphite from hyposulphate, trithionate and thiosulphate by the action of sodium amalgam, and on the synthesis of thiosulphate and trithionate from sulphite (*Chem. Soc. J.*, Abstr., **27**, 123; **28**, 129). 5. The conversion of sulphonates into sulphite and phenol on fusion with caustic alkali.

The relative instability of the sulphites is to be accounted for by the presence of the unoxidised metallic radicle. The oxidisability of moist or dissolved sulphur dioxide thus meets with an explanation:

being partly converted into sulphurous acid of the formula $HSO_2.OH$, it therefore contains unoxidised hydrogen.

If it be admitted that the sulphites are not dioxylic, there is no evidence of sulphur being sexvalent towards oxygen. The existence of Berthelot's compound, S_2O_7, which may appear to favour the view that sulphur is not quadrivalent but sexvalent, may fairly be doubted; considering the difficulties to be encountered in preparing and analysing such a body, it is not improbable that Berthelot dealt with a mixture of SO_3 with SO_4 or S_2O_5, the initial term of the series SO_3S (probably S_4O_6), SO_3Se, SO_3Te. Sulphur dioxide, the author thinks, should be represented by a formula in which the oxygen atoms are connected rather than by the formula O : S : O, which latter, however, must be regarded as established by the reaction: $OSO + PCl_5 = OSCl_2 + POCl_3$, but this stands alone.

The constitution of the various thionyl and sulphonyl compounds are fully discussed by the author on the hypothesis that sulphur is quadrivalent towards oxygen. He would define a sulphonate as an organic sulphite, and suggests that the sulphurous ethers, at present called sulphites, might be termed *thionites*.

In a similar manner the author endeavours to show that the properties of the metallic nitrites do not afford any grounds for supposing that they are oxylic salts. He calls attention to the large number of metallic derivatives that are known in which the metal is in direct association with nitrogen, and to the power that nitrogen has even to displace oxygen in some metallic oxides. He states that silver nitrite is but imperfectly acted upon by phosphorus oxychloride, no oxychloride of nitrogen being among the products; and that the fluorescence is destroyed on the addition of silver nitrite to a sulphuric acid solution of quinine. He refers to Russell's experiments on the action of hydrogen on silver nitrate as of special importance and as furnishing the facts in direct support of the view that nitrites are non-oxylic. They afford proof, as nearly as possible, that silver, although it cannot separate hydrogen from oxygen, yet separates it from nitrogen, and aided by this hydrogen then also dissolves in nitric acid itself: $2Ag + HNO_2 + HO.NO_2 = 2AgNO_2 + H_2O$. Nitrites are unlike nitro-bodies because of the presence in them of unoxidised metal. The nitrous ethers are not regarded as nitrites, and their formation along with the nitro-paraffins or true nitrites is attributed to the latter undergoing change at the moment of production.

If the nitrites be regarded as non-oxylic salts, there is no evidence that nitrogen is ever quinquivalent towards oxygen; and it may be regarded as probable that in the radicle NO_2 the two oxygen-atoms are associated together as well as with the nitrogen.

Discussion.

Prof. Odling regretted the impossibility of adequately discussing off-hand the many ingenious experiments and arguments set forth in the paper. The view taken by Dr. Divers as to the constitution of ordinary metallic sulphites and nitrites, had before now been put forward in a casual way, earliest in point of time, he believed, by himself; but this was the first occasion of its being, after full consideration, definitely advocated on the basis of experiment and interpretation of results. He would express his own unreserved concurrence with Dr. Divers to this extent, that, judged by their properties, ordinary metallic sulphites and nitrites presented on the whole a closer analogy to the variety of organic sulphites and nitrites commonly called sulphonates and nitro-compounds, than to the other variety of organic products to which the names sulphite and nitrite were more usually restricted. That the so-called sulphonates and nitro-compounds were essentially organic sulphites and nitrites, did not, in his opinion, admit of question, and he had long been in the habit of so representing them. He could not, however, go so far with Dr. Divers as to accept for a metallic sulphite or nitrite, the particular conception expressed in the one, to the entire exclusion of that expressed in the other, of the constitutional formulæ under discussion. To those chemists who looked upon structural formulæ as expressing the ascertained actual constitution of bodies, the alternative use of two inconsistent structural formulæ for one and the same body was an absurdity. But to those who, like himself, looked upon structural formulæ only as condensed expressions of the reactions of the bodies formulated, there was nothing absurd in the assignment of two or more inconsistent structural formulæ to one and the same body when manifesting what seemed to be inconsistent reactions. Many instances of so-called intramolecular transformation seemed to him only instances of reactions inconsistent with the expression of the constitution of the reagent by any such single structural formula as we were at present able to devise.

Dr. Wright said that he also preferred to use formulæ to represent particular reactions, and not as expressions of the actual constitution of bodies; he therefore saw no objection to the occasional use of inconsistent formulæ. The formulæ we were in the habit of using could not be true consitutional formulæ, for the mere reason that they represented the atoms as grouped in a single plane.

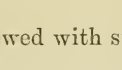
Prof. Tilden drew attention to the analogy existing between the sulphites and the carbonates; if the views of the author were admitted a very wide discussion would be opened. Isomeric sulphites should be possible, if Dr. Divers's formulæ were admissible.

Dr. Debus was inclined to question the validity of the arguments

put forward by Dr. Divers; after all, such questions were very much matters of opinion. As the action of ethyl iodide on silver nitrite gave rise to two isomeric compounds, it might be held that silver nitrite was a mixture; he, indeed, thought that probably there were two kinds of nitrites.

Dr. Armstrong said that the paper was of importance, as it must serve to call attention to the many points which await discussion relating to the chemistry of elements other than carbon. But he thought that in discussing questions such as were raised by Dr. Divers, we were treading upon very slippery ground; that we must recognise that it is very difficult to draw any definite conclusions regarding the "consitution" of compounds, such as are referred to, containing polyad elements, and especially associated *negative* polyad elements. We must admit that the molecules of such compounds are highly plastic; that they are characterised by great intramolecular mobility of their elements. Recent investigations have brought to light numerous remarkable cases of isomeric change among carbon compounds, and taking these into account, there can be little doubt that isomeric change will be found rampant when our methods of determining formulæ for compounds, other than those of carbon, are more advanced. Admitting the force of many of Dr. Divers's arguments, he would therefore object to go so far as Dr. Divers did, and would rather believe that in some cases the current belief, and in others that expressed by the author of the paper, was to be accepted; in other words, that all sulphites (and all nitrites) were not necessarily represented by one and the same formula. He could not agree with Prof. Odling and Dr. Wright, however, that it was permissible to assign two or more inconsistent formulæ to one and the same body. Regarding so-called constitutional formulæ as symbolic expressions of the chemical behaviour of compounds, it should be possible to devise for every compound a formula which would include all other less comprehensive expressions; our inability to do so in any case could only arise from want of knowledge of the compound, or from imperfection or incompleteness of the symbolic system. He thought that in considering these questions we are apt to take too formal a view; that we had fallen too fully under the control of constitutional formulæ; indeed, most, if not all, of Dr. Divers's arguments, might fairly be met by adversaries. Thus, assuming sulphites to be dioxylic, the action of $POCl_3$ may be represented as involving, in the first place, the formation of NaCl, SO_2 and P_2O_5, phosphate being then produced by the action of the P_2O_5 on an additional quantity of sulphite. In the production of thiosulphate, it might be supposed that by combination with sulphur the sulphite was converted into the compound $(NaO)_2SOS$, which then at once underwent isomeric change. With

reference to the oxidisability of sulphurous acid, he had more than once before contended that SO_2 was not oxidisable and sulphurous acid was, in consequence of the latter and not the former being an electrolyte; why the one and not the other was an electrolyte was an altogether different question.

Dr. Japp said that, speaking within the limits of the doctrine of valency, he viewed with suspicion the formula  assigned by Dr. Divers to sulphurous anhydride. This formula was a return to the devices adopted by the adherents of the dogma of constant valency when they wished to put the oxygen atoms out of court in determining the valency of polyad elements. The adherents of this view believed that the oxygen atoms in the oxides of polyad elements were capable of uniting with one another—of practising a species of collusion, in fact, to deceive the unwary chemist—and that their testimony was therefore untrustworthy. The *reductio ad absurdum* of the linked-oxygen view was to be found in the formulæ to which it led in the case of the perchlorates and periodates: thus potassium perchlorate would be written K—O—O—O—O—Cl, a formula which Kolbe happily compared to the result of Baron Münchhausen's feat of shooting ducks with his ramrod. This mode of uniting the oxygen atoms had, on further examination, broken down in almost every case where it had been adopted—even where, as in the case of the quinones, it had been adhered to with considerable obstinacy.

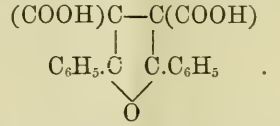
19. "The Illuminating Power of Hydrocarbons. I. Ethane and Propane." By Percy F. Frankland, Ph.D., B.Sc.

In continuing his researches on illuminating gas, the author has determined the illuminating power of ethane and propane. The gases were prepared by the action of the zinc-copper couple on ethyl and isopropyl iodides respectively, and then subjected to purification by passing them through bromine. The illuminating power of ethane, when consumed from a "referee's burner," at the rate of 5 cubic feet per hour, was found to be 34·8 candles, and that of propane 53·3 candles. The illuminating power of ethane is thus almost exactly half that of ethylene (68·5 candles), whilst that of propane is 1·5 times as great as that of ethane. From these results it appears that in the paraffin series of hydrocarbons, excluding the first member, methane, the illuminating power is directly proportional to the number of carbon atoms in the molecule.

20. "On Benzoylacetic Acid and some of its Derivatives." Part III. By Dr. W. H. Perkin, junr.

Ethylic dibenzoylsuccinate, obtained by treating ethylic benzoylsodacetate with iodine, crystallises from ether in needles melting at 129°. It is converted into a disodium derivative by the action of sodium ethoxide, from which apparently the sodium can be removed by means of iodine. *Dibenzoylsuccinic acid* is obtained by hydrolysis of the ethylic salt with alcoholic potash, but it is difficult to prepare.

On boiling ethylic dibenzoylacetate with dilute sulphuric acid, it is converted into an acid corresponding with Harrow's carbopyrotritaric acid: $C_{22}H_{22}O_6 + H_2O = C_{18}H_{12}O_5 + 2C_2H_6O$. This acid and a number of its salts are fully described. If treated with excess of acetic anhydride, it loses the elements of a molecule of water, being converted in a beautifully crystalline neutral body, $C_{18}H_{10}O_4$, which may be reconverted into the acid by means of alcoholic potash. The author regards the acid $C_{18}H_{12}O_5$ as *diphenylfurfurdicarboxylic* acid,



Ethylic benzoylsuccinate is obtained by the action of ethylic monochloracetate on ethylic benzoylsodacetate. If hydrolysed by boiling with concentrated baryta water, it yields benzoic and succinic acids; but if dilute sulphuric acid be used, benzoylpropionic acid and carbon dioxide are produced.

In the same way that ethylic acetoacetate is converted on heating into dehydracetic acid, so is ethylic benzoylacetate converted in a similar manner into the corresponding *dehydrobenzoylacetic acid*, $C_{18}H_{12}O_4 = 2C_{11}H_{12}O_3 - 2C_2H_5.OH$. If the heating be prolonged, other condensation products are obtained, two of which formed probably from 3 and 4 mols. of the acetate by withdrawal of the elements of 3 and 4 mols. of alcohol are described.

Dehydrobenzoylacetic acid crystallises in long yellow needles melting at 171—172°. It is a mon-acid; its salts, a number of which are described, are very stable. It does not combine with bromine; it is unaffected even after prolonged heating with acetic anhydride; but it is readily acted upon by phenylhydrazine. Ethylic dehydrobenzoylacetate, prepared from the silver salt and ethyl iodide, crystallises from benzene in almost colourless needles melting at 159°; it yields a (probably) mono-sodium derivative on treatment with sodium ethoxide.

Dehydrobenzoylacetic acid is converted into benzoylacetic acid by the action of alcoholic potash. On reduction with sodium amalgam, it yields an acid of the formula $C_{18}H_{14}O_4$, together with a small quantity of another of the formula $C_{18}H_{12}O_3$, or perhaps $C_{18}H_{14}O_3$. On

treatment with PCl_5, it yields a chlorinated compound, $C_{18}H_{11}ClO_3$, which is apparently a chlorinated acid of the formula $C_{17}H_{10}ClO.COOH$, and not an acid chloride.

The author fully discusses the bearing of his observations, and suggests as the most probable formula of dehydrobenzoylacetic acid the following: $\begin{matrix}(COOH)C.CO.CH\\ \| \quad \|\\ C_6H_5.C.\ O\ .C.C_6H_5\end{matrix}$. He supposes that, as in almost all cases of condensation of ethylic acetoacetate and benzoylacetate, the molecule first undergoes an internal change, the stable molecule $C_6H_5.CO.CH_2.COOEt$, becoming the "labile" $C_6H_5.C(OH):CH.COOEt$. (It is, I think, more probable that the condensation occurs under the influence of some minute impurity, which combines with the acetate, forming a compound that may be represented as

$$Ph.CY(OX).CH_2.COOEt;$$

from this point of view it is desirable to study the action of various "condensing" agents on ethylic acetyl and benzoylacetates, as a better yield of their dehydro-products may perhaps be thus obtained. —H. E. A.)

ADDITIONS TO THE LIBRARY.

I. *Donations.*

The New Chemistry. By J. P. Cooke. New York, 1884: from the Author.

Origine et Développement de la Chimie Organique: par C. Schorlemmer; traduit par A. Claparède. Paris, 1885: from Prof. Schorlemmer.

Pamphlets:—The Scientific and Literary Works of Dr. T. L. Phipson. By C. J. Bouverie: from the Author.

Observations on the Agricultural Chemistry of the Sugar-cane.

The Best Means of Detecting the Adulteration of Essential Oils.

Tentative d'empoisonnement par le Mercure. By T. L. Phipson: from the Author.

II. *By Purchase.*

Le Guide du Chimiste. Par M. Fremy and A. Terreil.

Life and Letters of Faraday. By Bence Jones. 2 vols.

Fragmentary Papers on Science and other Subjects. By Sir H. Holland, Bart.

Essays on Scientific and other Subjects. By Sir H. Holland, Bart.

Introduction to Chemical Philosophy. By J. F. Daniell.

How to Teach Chemistry. By E. Frankland.

Chemistry as Exemplifying the Wisdom and Beneficence of God. By G. Fownes.

The Chemist (complete set), 1840—1858.

The Chemistry of Vegetable and Animal Physiology. By G. J. Mülder. Part I.

The Elements of Chemistry. By D. B. Reid.

Organic Chemistry of Physiology and Pathology. By J. v. Liebig.

Chemistry of Agriculture and Physiology. By J. v. Liebig.

Researches on the Motion of the Juices in the Animal Body. By J. v. Liebig.

Treatise on Poisons. By R. Christison.

London Dispensatory. By A. T. Thomson.

Companion to the British Pharmacopœia. By P. Squire.

The Chemistry of Common Life. By J. F. W. Johnston. 2 vols.

A Treatise on Food and Dietetics. By F. W. Pavy.

On Food. By H. Letheby.

Adulterations Detected in Food and Medicine. By A. H. Hassall.

Chemical Analysis. By J. G. Children.

Chemical Analysis. By C. R. Fresenius; translated by J. L. Bullock.

Outlines of Qualitative Analysis. By H. Will.

How to Work with the Spectroscope. By J. Browning.

The Use of the Blowpipe. By J. J. Berzelius.

The Use of the Blowpipe. By J. S. Muspratt.

The Practical Assayer. By O. North.

Laboratory Teaching. By C. L. Bloxam.

Chemical Technology. By R. Wagner.

Inorganic Analysis. By F. Wöhler.

On Colour. By E. Chevreul.

Titles of Papers of interest to Chemists recently read before Societies in the United Kingdom:—

"On the Atomic Weight of Glucinum (Beryllium)." No. II. By Prof. Humpidge.

"On the Extraction of Uric Acid Crystals from the Green Gland of *Astacus fluviatilis*." By Dr. A. B. Griffiths.

Royal Society of London, March 5th.

"Ammonia from the Nitrogen of Minerals." By G. Beilby.

"Tempered Glass." By Frederick Siemens.

Society of Arts, Feb. 12th and 26th.

HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY, ST. MARTIN'S LANE.

ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 5. Session 1884-85.

March 19th, 1885.—Dr. W. H. Perkin, F.R.S., President, in the Chair.

Messrs. C. J. Baker, H. Brereton Baker and George Patterson were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Harold Follows, The Hough, Stafford; Harry M. Freear, 40, Osborne Road, Tollington Park, N.; F. A. Genth, Jun., 4014, Chesnut Street W., Philadelphia, U.S.A.; G. M. Gregory, Gazipur, N.W.P. India; and William Hamilton Reid, 20, Wharf Street, Stockton-on-Tees.

Addendum to Discussion on Paper No. 18.

Dr. Debus wishes to have pointed out that the statement attributed to him that "after all, such questions were very much matters of opinion" is based on a misunderstanding of his remarks; that he certainly does not hold the views which can be deduced from such a statement, as chemical research in our days is carried on by the majority of chemists—perhaps 99 in 100—on the assumption that the mode of combination of atoms in molecules *can* be made out. He only differs from Dr. Divers in one point: in not considering the experiments of Dr. Divers as sufficient evidence that the metal in nitrites is in direct combination with nitrogen. We must conclude from the formation from silver nitrite of nitroethane together with ethyl nitrite, that silver nitrite is a mixture of two salts; *but* silver nitrite and methyl iodide yield *only* nitromethane.

The following papers were read:—

21. "On the Presence of Choline on Hops." By Dr. Griess, F.R.S., and Dr. G. H. Harrow.

The authors have separated choline, $C_2H_4(OH).NMe_3.OH$, from hops by adding to a concentrated extract, acidified with chlorhydric acid, a solution of iodine in iodhydric acid. The semi-solid precipitate obtained—a choline periodide—was boiled with water to expel iodine, and the resulting solution of choline iodide treated with silver oxide; the impure choline in the solution was then converted into the auro-chloride, which was recrystallised. In this manner they have not been able to obtain more than 1—50th per cent. of choline from hops. They consider it not improbable that it exists in loose combination with resin, as they find that a very dilute aqueous solution is capable of dissolving comparatively large quantities of hop resin, the liquid being then of intensely bitter taste. Employing the same method, they have also extracted choline from beer.

22. "Fluorene." Part III. By Dr. W. R. Hodgkinson.

In two previous notes to the Society, the author has remarked upon, and given examples of, the facility with which fluorene and its derivatives condense to a double molecule, owing to the presence of the CH_2-group. This action takes place when fluorene is heated to a high temperature alone or in contact with even very gentle oxidising agents. In a previous note, two isomeric difluorenes were described, which were obtained from the red body produced when fluorene is passed over red-hot manganese dioxide. At that time the red body was distilled under reduced pressure, as the red colour could not be removed by crystallisation, and the distillate was then crystallised from acetic acid. It has since been found that the hydrocarbon, $C_{26}H_{18}$ (melting at 246°), termed *para-difluoryl*, suffers considerable, if not complete, decomposition even when distilled under reduced pressure. However, by distilling the crude product only so far as to separate the main bulk of unaltered fluorene, and treating the highly-coloured residue with cooled ether—which dissolves the red colouring matter and any unchanged fluorene—a very slightly coloured residue of the $C_{26}H_{18}$ hydrocarbons is obtained. The crude product forms about 10 per cent. of the original fluorene, and contains at least three isomers of the formula $C_{26}H_{18}$. The one present in greatest quantity, and the only one as yet examined, is that melting at 246°. This body forms long prisms, very slightly soluble in cold ether or chloroform, and only moderately in hot acetic acid. On slightly heating it above its melting point, it decomposes, forming another hydrocarbon of lower melting point, and a large amount of carbonaceous matter. It is not easily brominated; a cold solution in $CHCl_3$ may be treated with bromine without much action taking place, and, when heated, a tetrabromo-compound, extremely insoluble in all solvents, is formed, which melts, with decomposition, at about 302°. On boiling it with

fuming nitric, a di-nitro-compound is formed. It is not very easily oxidised; the acetic solution requires to be boiled with a large excess of CrO_3. The product crystallises from acetic acid in very fine rhombs, melting at 255°, and sublimes unchanged. It has the composition $C_{26}H_{14}O_2$, and is probably an oxide, not a quinone. Alkalis, bromine, or nitric acid scarcely affect it.

The di-haloïd derivatives of fluorene, as mentioned in the author's previous note, contrary to statements by Van Dorp and others, are readily acted upon by alkalis, halogen being removed and difluorene compounds formed; with fused or concentrated potash the action is violent, and pure products are not easily obtained. The action of alcoholic potash is more manageable, but the best result is obtained by the action of sodium ethoxide. On dissolving $C_{13}H_8Br_2$ in alcohol, and adding sodium, a green solution is formed; on dilution with water and boiling, this deposits a brilliant red crystalline powder, which is exceedingly insoluble. Analysis shows it to have the composition $C_{26}H_{14}Br_2O$. This body crystallises from boiling cumene or acetic anhydride in red microscopic prisms, melting above 360°; the chloro-derivative is analogous.

It appeared possible that this body might be produced by the simultaneous action of bromine and potash on fluorene; it was found, however, that the main product is monobromofluorene, identical with that already described, melting at 103—104°; this is an excellent way of making the mono-haloid derivatives of fluorene, as in the ordinary way much di-haloïd derivative is always formed. Sodium ethoxide acts on monobromofluorene; the product is of a yellow colour and free from bromine.

A mononitrofluorene is obtained by very careful addition of the calculated amount of nitric acid to a cooled solution of fluorene in acetic acid; it forms small prisms, very soluble in hot alcohol, and melts at 151°. The amido-compound from it is rather unstable. On heating nitrofluorene above its melting point, it decomposes, one product being a $C_{26}H_{10}$ hydrocarbon that is not identical with any of those directly obtained from fluorene.

23. "Combustion in Dried Gases." By H. Brereton Baker, B.A.

Led by Mr. Dixon's experiments, the author has investigated the question whether moisture is necessary for the combustion of carbon and phosphorus in oxygen. The phosphorus used (commercial amorphous phosphorus) had been washed with water and dried at 100° in a current of carbon dioxide previously passed through two wash-bottles of sulphuric acid; it was then heated in a Sprengel vacuum, at 150—160°. The carbon (finely powdered charcoal) had been heated

to bright redness in a current of dried chlorine for three hours; the tube containing it was then transferred to an air-bath and heated at 200° while a current of dried air was passed through it. Portions (0·5—1 gram) were sealed up in bent hard glass tubes along with phosphoric oxide, the tube being filled with oxygen prior to sealing; to free the glass from adhering moisture, the ends of the tubes containing the carbon or phosphorus were heated in an air-bath at 130—150°, the other ends being kept cool. After about eight days, the tube containing phosphorus and dried oxygen and another similar tube with phosphorus in oxygen saturated with water were supported at the same height above the flame of an Argand burner: the phosphorus in the wet gas soon took fire, but that in the dried gas slowly distilled and formed a red and yellow deposit on the cooler part of the tube. A similar pair of tubes containing carbon was placed over the large flame of a Bunsen burner: the moist carbon burnt with bright scintillating flashes, but no apparent combustion took place in the tube containing dried gas, though it was heated to bright redness for several minutes.

A series of such experiments with carbon were then made, in which the drying extended over various periods, the gaseous contents of the tubes being analysed after the tubes were heated. The results obtained clearly show that the burning of carbon is much retarded by drying the oxygen to the extent which is possible with the arrangement adopted by the author.

	Wet.	Dried 1 week.	Wet.	Dried 2 weeks.	Wet.	Dried 4 weeks.	Wet.	Dried 8 weeks.	Wet.	Dried 12 weeks.	Wet.	Dried 16 weeks.
CO_2 ...	50·1	15·4	51·0	19·0	45·3	14·1	23·3	12·5	58·8	15·8	52·4	17·8
CO	22·2	20·6	31·2	14·8	32·5	27·8	60·0	27·5	23·2	24·2	25·2	16·5
O_2	—	41·3	—	46·1	—	28·2	—	39·0	—	33·3	—	45·0
N_2	27·6	22·6	17·7	20·0	22·1	29·8	16·6	21·0	17·9	26·6	22·3	20·6

Other forms of the experiment were described, which led to similar results.

The author successfully made an experiment before the Society with two tubes, the one containing dried, the other undried, oxygen and carbon.

Discussion.

Referring to Mr. Cowper's experiments, Dr. Debus said, that the fact that Dutch metal did not take fire in dry chlorine might be due

to the formation of a protecting layer of chloride; if water were present, this would become dissolved. Such an explanation, however, cannot hold good for gases.

He described some experiments made at his suggestion by Mr. Cowper with a view to test some of the conclusions arrived at by Mr. Dixon in his research on the explosion of mixtures of carbonic oxide and oxygen.

The heat of combustion of carbonic oxide at 18°, according to Thomsen, is 67,960 units; the heat of formation of water-vapour at 100° is 58,069 units, and accordingly at 18° it is 58,778 units; hence the thermal change involved in the burning of carbonic oxide at the expense of the oxygen of water is 67,960 — 58,778 = 9,182 units.

Therefore, it appears theoretically more probable that the carbonic oxide of a mixture of carbonic oxide, oxygen, and moisture will, during combustion, combine with free oxygen rather than with the oxygen of the aqueous vapour.

Mr. Cowper's experiments, however, confirm Mr. Dixon's statement that a mixture of dry carbonic oxide and oxygen is not exploded by the passage of electric sparks, but he observed that a slow and partial combination of the gases takes place, probably caused by the high temperature of the platinum wires between which the sparks were produced. Mr. Baker has shown that the combustion of dry charcoal in dry oxygen is incomplete and much slower than in ordinary moist oxygen. Hence, moisture appears to play in the combustion of solids the same part as it does in that of gases. Mixtures of hydrogen and oxygen, however dry, always exploded.

Dr. Armstrong regarded Mr. Baker's paper as an important addition to our knowledge. By facts such as those adduced, chemists must ere long be led to form a definite conception of the nature of chemical action and of the conditions under which chemical action could take place. It was well known that iron did *not* rust in oxygen; that zinc did *not* dissolve in diluted sulphuric acid; that chlorine did *not* affect sodium. These facts had led him a good many years ago to come to the conclusion in his own mind that probably chemical action did not take place between *two* substances, and numerous facts which had since come to light had only served to strengthen this conviction: for example, those afforded by Mr. Cowper's observations on the behaviour of metals in dry chlorine, and by Mr. Dixon's refined study of the conditions under which carbonic oxide explodes. He had even ventured to affirm to Mr. Dixon that some day it would be ascertained that a mixture of pure oxygen with pure hydrogen was not explosive. It should be pointed out, however, that although chemists had failed to formulate any definite conception regarding chemical action, physicists had already pointed out that the amount of

chemical action that could occur between *two* substances was practically *nil*, this having been stated in so many words by Ayrton and Perry in their paper on the "Contact Theory of Voltaic Action" (*Proc. Roy. Soc.*, 1878, **27**, 196). Dr. Armstrong said that the view which he now held was best stated by defining chemical action as *reversed electrolysis*, *i.e.*, in any case in which chemical action was to take place, it was essential that the system operated upon should contain a material of the nature of an electrolyte. Neither oxygen nor hydrogen was an electrolyte, therefore a mixture of only these two gases should not be explosive; a mixture of pure oxygen and pure carbonic oxide for like reasons should not explode. There was, however, a tendency perhaps to exaggerate the importance of water and to overlook the possible presence in minute quantity, and influence of, other bodies. Water not being an electrolyte, as it was scarcely probable that water and oxygen or hydrogen would form an electrolyte, it was difficult to understand that the presence of water pure and simple should be of influence in the case of a mixture of oxygen and hydrogen. It was, perhaps, necessary to distinguish two kinds—or degrees—of chemical action: that taking place at moderate, and that taking place at high temperatures. It may be that on passing sparks in a mixture consisting only of carbonic oxide and oxygen, oxidation takes place in the path of the sparks but is not propagated throughout the mass—*i.e.*, there is no explosion—on account of the excessive resistance. ["To connect the two ideas (of chemical affinity and the amount of chemical action) we have a third, viz., resistance, and the electrical law of Ohm becomes the chemical law—the quantity of chemical action in unit time equals the sum of a great number of terms, each of which is an electromotive force divided by a resistance."—Ayrton and Perry, *loc. cit.*]

Dr. Alder Wright remarked that the appearance described by Dr. Debus (as observed by Mr. Cowper in his repetition of Mr. Dixon's experiment with dried carbonic oxide and oxygen) of a slight amount of blue flame in the vicinity of the platinum wires, indicating a small amount of chemical action not propagated throughout the whole mass, appeared to him to be connected with the fact that a stream of purified CO (not dried), issuing from a gasholder with more than a certain limiting velocity, will not burn with a continuous flame, but blows itself out, the velocity of propagation of chemical action in the mixture of CO and air formed at the orifice from which the CO issues in the outer portion of the stream being less than the onward velocity of the moving stream. It would be of interest to determine the limiting velocity at which the gas would just cease to burn for different degrees of dryness, and the influence of such conditions as temperature and pressure upon the velocity: or mixtures of CO and

O_2 might be burnt (from a safety jet) with varying speeds of delivery and of various degrees of dryness. With reference to the views of Dr. Armstrong respecting the intimate connection between chemical action and electrical phenomena, it might be of interest to recall the fact that in 1841 and subsequent years, Dr. J. P. Joule put forth this creed (in a series of papers in the *Phil. Mag.*), that the development of heat in combustion and analogous chemical phenomena resulting in the formation of electrolytes is simply a consequence of resistance to electric conduction between the particles of the bodies undergoing change, so that the heat evolved in such actions is proportional to the electromotive force of the current passing between the particles. This view and the consideration of later valuations of certain heats of chemical change was subsequently (1851) expanded by Sir W. Thomson in his well known paper on the "Mechanical Theory of Electrolysis," in which it was shown that the actual electromotive force generated by a Daniell cell was directly calculable in absolute units from the heat development brought about in virtue of the sum of the chemical changes taking place in the cell whilst in action; and although subsequent investigations have shown that with certain kinds of voltaic combinations the agreement between the observed and calculated electromotive force is not as close as with the Daniell cell, yet on the whole it may fairly be regarded now as distinctly proved that the possibility of the occurrence of chemical change, and the way in which it takes place, are most intimately associated with certain of the electrical qualities of the bodies brought together.

Mr. Crookes said that in making incandescent lamps he had noticed some facts of interest in connection with the paper. During exhaustion, the filament was heated first to a moderate extent in carbon tetrachloride vapour, and afterwards, when a very high exhaustion was attained, to a very high temperature. Lamps thus prepared had been found sometimes to last in use for a great many hours, even when some oxygen was present in the bulbs; but at other times they very soon broke down: at last it was discovered that in the latter case the phosphoric oxide in the drying tubes attached to the pump had deliquesced. It was practically impossible to dry gases with sulphuric acid, and it was almost as difficult to do so with phosphoric oxide; he had only succeeded by passing the gas through six feet of combustion tubing into which phosphoric oxide had been tightly packed.

Mr. Vernon Harcourt said that oxygen inclosed with phosphoric oxide for many days would probably become as nearly dry as oxygen passed through a long tube tightly packed with the same substance. Mr. Dixon had found that the inflammation of a mixture of oxygen

and carbonic oxide depended upon the pressure and temperature to which the gases were subjected, as well as upon the proportion of steam mixed with them. A nearly dry mixture, uninflammable by the electric spark under a pressure of half an atmosphere, might be inflamed by a stream of sparks or under a greater pressure. A mixture of hydrogen and oxygen could be inflamed by the electric spark only at a certain tension, and this tension was the same whether steam were present or, as far as possible, absent. Perhaps in this case also some third substance was present. The action of steam was not likely to be exceptional. Mr. Baker seems to have established the conclusion which he had expressed with proper caution, that the combination of carbon and oxygen is affected by the presence of steam.

Titles of Papers of interest to Chemists recently read before Societies in the United Kingdom:—

"The Absorption Spectra of the Alkaloïds. II." By Prof. W. N. Hartley, F.R.S.

"Contributions towards the Solution of the Chemical Constitution of Isatin." By the late Prof. H. Kolbe, For. Mem. R.S.

"On Transfer-Resistance in Electrolytic and Voltaic Cells." By Dr. Gore, F.R.S.

"On the 'Paralytic' Secretion of Saliva." By J. N. Langley, F.R.S.

Royal Society of London, March 12th and 19th.

1. "Hooke's Anticipations of the Kinetic Theory and of Synchronism." By Prof. Tait.

2. "On the Hexagonal System in Crystallography." By Prof. Crum Brown.

3. "On the Effect of Temperature on the Compressibility of Water." By Prof. Tait.

Royal Society of Edinburgh, March 16th.

NOTICE TO AUTHORS OF PAPERS.

To facilitate the preparation of these "Abstracts of Proceedings," all authors are requested to furnish abstracts of their communications, and to send their papers so that they may be in the hands of the Secretaries, if possible, on the Monday before the day of meeting.

The Anniversary Meeting will be held on Monday, March 30th, at 8 o'clock.

(*The 31st has been incorrectly announced on the Balloting Papers.*)

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 6. Session 1884-85.

March 30th, 1885.—Annual General Meeting. Dr. W. H. Perkin, F.R.S., President, in the Chair.

The President read an address, of which the following is a brief abstract:—

The number of Fellows is now 1,360, being an increase of 34 since March 31st, 1884. The losses have been exceptionally heavy, 4 Honorary Foreign Members, Victor Dessaignes, Adolph Wurtz, Jean Baptiste Dumas, and Hermann Kolbe having died during the year, besides 18 Fellows: G. D. Atkinson, Adrian Blaikie, James Forrest, Robert Harvey, J. W. Hudson, F. M. Jennings, Robert Jones, M. J. Lansdell, James Napier, H. B. Pritchard, T. K. Rogers, Juwansnigji Jarwatsnigje, R. Angus Smith, J. L. Shuter, Sidney Gilchrist Thomas, A. Voelcker, Henry Watts, and G. W. Wigner. 32 Fellows have either withdrawn or have been struck off the list as being in arrear of their subscriptions.

After speaking of the great loss which the Society had experienced in Mr. Watts, the President referred to the appointment of Mr. C. E. Groves, F.R.S., as Editor; of Mr. A. J. Greenaway, as Sub-Editor; and Dr. L. T. Thorne, as Librarian.

Very considerable additions have been made to the Library, and the thanks of the Society are due to Fellows who have responded to the appeal for copies of old editions to complete series of standard works. The Library is increasing so fast that additional accommodation will soon be a necessity. It is expected that the complete subject catalogue will be issued before long.

Reference was next made to the Society's new publication—the "Abstracts of Proceedings," and to the Reception held by the President and Council; a second Reception will be held later in the session.

The chief chemical work of the year was then passed in review.

Last year, the President referred in his address to the comparatively small amount of original work which was being prosecuted in this country, notwithstanding the increased number of laboratories, and the greater facilities which were offered for the encouragement of research. The number of papers brought before the Society during the year is 67, but although the number has not increased, if the papers themselves be examined, it will be found, the President thinks, that the amount of work done is somewhat larger, though certainly not so large as it should be. It is to be hoped that the spirit of research will be stimulated in the laboratories of the kingdom, and that men may be turned out who are not only more or less qualified analysts, but thorough chemists. "Let us not," said the President, "be content with looking back with pride to what our ancestors have done, but let us follow their example."

It was then moved by Dr. GLADSTONE, and seconded by Sir F. A. ABEL, that the best thanks of the meeting be given to the President for his address, and that he be requested to allow it to be printed. This resolution was unanimously accepted, and the President returned his thanks.

Dr. RUSSELL, the Treasurer, then read his report:—The income of the Society for the year was about £3,569, the expenditure £3,283, leaving a balance of only £286; about £2,198 had been expended on account of the Journal, and about £440 on account of the Library.

Mr. MOND proposed, and Mr. MAKINS seconded, a vote of thanks to the Treasurer, to which Dr. RUSSELL replied.

Mr. FRISWELL proposed, and Mr. G. S. JOHNSON seconded, a vote of thanks to the Auditors, Mr. Makins, Mr. R. H. Davies, and Dr. P. F. Frankland. Mr. MAKINS replied.

A vote of thanks to the Officers and Council was then proposed by Mr. WARINGTON, seconded by Mr. RILEY, and replied to by Dr. ARMSTRONG.

Mr. TYRER proposed, and Dr. JAPP seconded, a vote of thanks to the Editor, Sub-Editor, Abstractors, and Librarian. Mr. GREENAWAY replied.

Dr. Plympton and Mr. E. W. Voelcker were appointed scrutineers, and a Ballot having been held, the following were declared elected as Officers and Council for the ensuing year:—

President: Dr. Hugo Müller.

Vice-Presidents who have filled the office of President: Sir F. Abel, Dr. Warren De la Rue, Prof. Frankland, Dr. J. H. Gilbert, Dr. J. H. Gladstone, Dr. A. W. Hofmann, Prof. Odling, Dr. W. H. Perkin, Sir Lyon Playfair, Sir Henry Roscoe, and Prof. A. W. Williamson.

Vice-Presidents: Mr. W. Crookes, Prof. G. D. Liveing, Dr. Schunck, Prof. T. E. Thorpe, Dr. Tilden, and Mr. Walter Weldon.

Secretaries: Dr. H. E. Armstrong and Mr. John M. Thomson.

Foreign Secretary: Dr. F. R. Japp.

Treasurer: Dr. W. J. Russell.

Ordinary Members of Council: Dr. E. Atkinson, Mr. H. T. Brown, Dr. Carnelley, Mr. Carteighe, Dr. F. Clowes, Mr. A. E. Fletcher, Prof. G. C. Foster, Mr. Friswell, Mr. Meldola, Dr. Messel, Mr. Ludwig Mond, and Mr. C. O'Sullivan.

April 2nd, 1885.—Dr. H. Müller, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. Edward Grindle Hogg, Sandringham Gardens, Ealing; F. R. Mallet, Calcutta; John A. Tate, 33, Selborne Street, Liverpool.

The following papers were read:—

24. "On the Formation of Hyponitrites from Nitric Oxide." By Prof. Divers and T. Haga.

An alkaline solution of potassium stannite slowly absorbs nitric oxide, and when treated with silver nitrate gives a precipitate from which by treatment with nitric acid and ammonia, silver hyponitrite can be obtained in small quantity. Potassium stannite in alkaline solution has no action on nitrites and nitrates. Ferrous hydroxide treated with strong solution of alkali, becomes dense, pulverulent, and pale grey, and in taking up oxygen does not form any black hydroxide as an intermediate product. Ferrous hydroxide mixed with potassium hydroxide solution, converts nitric oxide, and also nitrites, into ammonia. It has no action upon nitrates in presence of much potassium hydroxide.

25. "On the Existence of Barium and Lead Nitrososulphates." By Prof. E. Divers and T. Haga.

Barium nitrososulphate can be precipitated from an alkali nitrososulphate by barium hydroxide if concentrated solutions are used. It is soluble in water, and decomposed by acids. Lead nitrososulphate mixed with hydroxide is precipitated from a nitrososulphate solution by adding basic acetate of lead to it.

Before this, attempts to form other nitrososulphates than those of the alkalis have proved unsuccessful.

36. "Notes on Fractional Distillation in a Current of Steam." By Dr. M. G. Lazarus.

Difficulty having been experienced in the separation of iodothiotolen and iodothioxen from toluene and xylene respectively, owing to the two former compounds being almost totally decomposed on distillation even under reduced pressure, experiments were made to ascertain whether a separation could be effected by distilling in a current of steam. Mixtures of benzene and toluene, benzene and nitrobenzene, toluene and nitrobenzene, toluene and xylene, benzene and carbon bisulphide, turpentine and nitrobenzene, and aniline and nitrobenzene were employed. A perfect separation could not in every case be effected, but the results are so far satisfactory as to render the method of practical use, and it was found that pure iodothiotolen and iodothioxen could be obtained by it.

Discussion.

Dr. Perkin remarked that if he understood the authors' remarks correctly, the methods employed would yield the best results with mixtures of liquids differing considerably in their densities, and stated that this had been his own experience.

The President stated that his experience had been similar to that found by Dr. Perkin.

27. "Derivatives of Taurine." Part I. By J. W. James.

The author has investigated the action of mono-, di-, and tri-amines on the corresponding salts of β-chlorethanesulphonic acid, and in this way prepared mono-, di-, and tri-substituted derivatives of taurine (β-amidoethylsulphonic acid).

The method consists in heating the substituted ammonium salt of the acid with the calculated quantity of amine in a closed tube for ten hours at 160°, when the taurine-derivative is formed, mixed with the hydrochloride of the base. For mono- and di-derivatives the following method was employed in separating the hydrochloride. The contents of the tube were treated with an excess of barium hydrate, and steam was passed in until all the amine had distilled off. The barium was then removed by pouring the boiling solution into the calculated quantity of boiling dilute sulphuric acid; after filtering from $BaSO_4$, the solution was evaporated, leaving the substituted taurine.

Trimethyltaurine being easily decomposed by dilute solution of alkalis, barium hydrate could not be employed; it was, however, readily obtained in a state of purity by boiling the mixture of tri-

methyltaurine and trimethylammonium chloride with strong alcohol, which dissolved only the chloride.

In this manner *ethyl-*, *allyl-*, *phenyl-*, *dimethyl-*, *diethyl-*, *methylphenyl-*, and *trimethyl-taurines* have been prepared. They are beautifully crystalline substances, all of which dissolve in water and alcohol, with the exception of trimethyltaurine, which is insoluble in the latter liquid.

The di-substituted taurines are of special interest, as corresponding compounds in the carboxyl series are not known. The mono- and di-taurines form no compounds with acids or platinum chloride, and in this respect are sharply distinguished from the corresponding derivatives of amido-acetic and propionic acids. The mono- and di-derivatives have an acid reaction (J. Lang, *Bull. Soc. Chim.* [2], **25**, 80). Trimethyltaurine is perfectly neutral to litmus.

The action of cyanamide has also been studied, and phenyltaurocyamine and dimethyltaurocyamine have been prepared. They are crystalline substances, soluble in water.

Discussion.

The President remarked that as we have in taurin, or amidethylsulphonic acid, the basic and acid properties so nearly balanced, it might have been expected that by a farther introduction of alcohol radicles the alkaline character would become more pronounced. According to the results of the author, however, this does not appear to be the case.

28. "On the Preparation of Ethylene Chlorothiocyanate and β-Chlorethanesulphonic Acid." By J. W. James.

It is found that a much better yield of the thiocyanate is obtained by distilling the product of the action of potassium thiocyanate on ethylene chlorobromide under reduced pressure.

Pure chlorethanesulphonic acid can only be prepared by treating the barium salt with sulphuric acid; even when very dilute solutions of the lead salt are treated with sulphuretted hydrogen, some lead always remains dissolved.

29. "The Orthovanadates of Sodium and their Analogues." By Harry Baker, Berkeley Fellow, Owens College.

Though vanadium belongs to the phosphorus, arsenic, niobium, and tantalum-group of elements, the number of points of resemblance between their compounds is not very great; and indeed Mendelejeff remarks that the analogues of vanadium are titanium and chromium, and niobium and tantalum, to which latter it shows greater resem-

blance than to phosphorus; and Rammelsberg, after examining numerous vanadates, concludes that they cannot be compared with the phosphates. In a previous paper to this Society I described certain unsuccessful experiments which had for their object the preparation of fluoxyvanadates isomorphous with the fluoxyniobates. In order to trace the resemblance between the vanadates, phosphates, and arsenates, it is evidently necessary to confine attention to the tribasic ortho-salts, since acid ortho-vanadates cannot be prepared, and on the other hand the pyro- and meta-arsenates are not known in the crystalline state. The only tribasic orthovanadates, phosphates or arsenates soluble in water, are those of the two alkalis sodium and potassium, and of these only sodium is available, since the potassium salts crystallise with great difficulty. A careful examination of the sodium vanadates was therefore undertaken with the view of comparison, and with good success; for out of the four hydrates of the above salt described in this communication, viz.—

(1.) $Na_3VO_4.12H_2O$, hexagonal prisms,
(2.) $Na_3VO_4.10H_2O$, rhombic dodecahedra,
(3.) $Na_3VO_4.10H_2O$, hexagonal plates,
(4.) $Na_3VO_4.8(?)H_2O$, rhombic plates,

salts exist in the phosphorus and arsenic series exactly corresponding to three of the vanadates, viz., Nos. 1, 2, and 4. Double salts of sodium phosphate with sodium fluoride have several times been described, which *all* crystallise in regular octohedra, though remarkably different compositions are ascribed to them. These descriptions, however, all apply to one and the same body, and it is shown in the paper that to this there are exactly corresponding salts containing in place of phosphorus, arsenic and vanadium, thus: $2Na_3VO_4.NaF.19H_2O$. From these experiments the conclusion is evident that the salts of vanadic acid are not, as would appear, entirely different to those formed by phosphoric and arsenic acids, but do exactly resemble them in those cases where corresponding members are known.

Discussion.

The President thought that the arguments brought forward by Mendelejeff and also by Rammelsberg in favour of placing vanadium along with molybdenum and chromium, seem hardly strong enough to assail the position which Roscoe's researches have assigned to it in the periodic system, and according to which it is classed along with phosphorus and arsenic. The results of the author's researches seem to afford a farther confirmation; and, indeed, no other proof appears in this respect so convincing as the comparison of the three minerals —pyromorphite, mimetesite, and vanadinite.

ADDITIONS TO THE LIBRARY.

Donations.

The New Chemistry. By J. P. Cooke. Revised edition: New York, 1884: from the Author.

Chimie Organique: par C. Schorlemmer; traduit par A. Claparède. Paris, 1885: from Prof. Schorlemmer.

International Electric and Gas Exhibition at the Crystal Palace, 1882–3. Report on the Gas Section; 2 vols.; London, 1884: from the Gas Institute.

The Alkali-makers' Pocket Book. By George Lunge and F. Hurter; London, 1884: from the Publishers.

By Purchase.

Researches on Magnetism. By Baron v. Reichenbach.
Mineralogy. By R. Jameson. 3 vols.
Elements of Mineralogy. By J. Nicol.
Die Metéorite. By P. Partsch.
Mineralogist's Directory. By T. M. Hall.
Manual of Mineralogy. By J. Nicol.
Manual of Mineralogy. By J. D. Dana.
Mineralogy and Geology. By T. Thomson.
Electricity and Magnetism. By J. Cuthbertson.
Lectures on Electricity. By H. M. Noad.
Heat a Mode of Motion. By J. Tyndall.
Special Loan Collection, 1876: Catalogue.
Admiralty Manual of Scientific Enquiry.
Electric Illumination. By J. Dredge: London, 1885.

Strecker's Text-book of Organic Chemistry. By Johannes Wislicenus; translated and edited by W. R. Hodgkinson and A. J. Greenaway: London, 1881.

A Handbook of Organic Chemistry. By William Gregory: London, 1852.

Religio Chemici. By George Wilson: London, 1862.

The Urine in Health and Disease. By A. H. Hassall: London, 1863.

Chemistry of Agriculture and Physiology. By J. v. Liebig: London, 1843.

Bread Analysis. By J. A. Wanklyn and W. J. Cooper: London, 1881.

Manual of the Metalloïds. By J. Apjohn: London, 1864.

Familiar Letters on Chemistry. By J. v. Liebig: London, 1851.

Rural Chemistry. By E. Solly: London, 1846.

Méthode de Nomenclature Chimique. Par MM. Hassenfratz et Adet: Paris, 1787.

Chimie Moderne. Par Ad. Wurtz: Paris, 1879.

Abstracts of Lectures delivered at the Royal Institution. By William Odling.

Elementary Chemistry. By H. M. Hart: London, 1870.

Das Cyan und seine anorganischen Verbindungen nebst dem Mellon. By O. B. Kühn: Leipzig, 1863.

Metals. By C. L. Bloxam: London, 1870.

Éléments de Physique et de Météorologie. Par M. Pouillet: Paris, 1837.

The Industrial Resources of the Tyne, Wear, and Tees. Edited by Sir W. G. Armstrong, I. L. Bell, J. Taylor, and Dr. Richardson: Newcastle-on-Tyne, 1864.

Telegraphy. By W. H. Preece and J. Sievewright: London, 1876.

NOTICE TO AUTHORS OF PAPERS.

To facilitate the preparation of these "Abstracts of Proceedings," all authors are requested to furnish abstracts of their communications, and to send their papers so that they may be in the hands of the Secretaries, if possible, on the Monday before the day of meeting.

Titles of Papers of interest to Chemists recently read before Societies in the United Kingdom:—

"Observations on Variations of the Electromotive Force between Metals at High Temperatures in Fused Salts." By Thos. Andrews.
Royal Society of London, March 26th.

"On the Seat of Electromotive Force in a Voltaic Cell." By Prof. O. G. Lodge.
Society of Telegraph Engineers, March 26th.

The next Meeting of the Society will be held on Thursday, April 16th, when there will be a ballot for the election of Fellows.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 7. Session 1884-85.

April 16th, 1885.—Dr. W. H. Perkin, F.R.S., Vice-President, in the Chair.

Certificates were read for the first time in favour of Messrs. Thomas J. Greenway, 28, Wilkinson Street, Sheffield; Harry Haslett, Chatham Brewery, Chatham; Arthur Richardson, 35, Canynge Square, Clifton.

The following papers were read :—

30. "A Crystalline Tricupric Sulphate." By W. H. Shenstone.

When crystals of copper sulphate and a little water, or the crystals of copper sulphate alone, are heated up to temperatures approaching 200° C., masses of minute emerald-green crystals are formed. They are insoluble in water, and give on analysis numbers which lead to the formula $CuSO_4 2CuH_2O_2$.

An account of their chief characters is given.

Mr. H. H. Miers, M.A., has examined and reports on their crystallography. The crystals are on the rhombic system. They exhibit no evident relation to brochantite.

31. "A Modified Bunsen Burner." By W. H. Shenstone.

A description of a form of Bunsen burner in which a ring of small or large flames can be made to play upon the crucible to be heated. The arrangement can be adjusted so as to apply the heat, from above, to the surface of liquids, so that evaporation, &c., in analytical operations can be more easily carried on without spurting. It may also be used to ignite at any desired temperature in the ordinary way.

32. "The Chlorination of Phloroglucol."

The author has studied the chlorination of phloroglucol in suspen-

sion in carbon tetrachloride, at temperatures below zero. Under these circumstances he finds that the chlorination of the phenol precedes, as a distinct stage in the reaction, the disruption of the benzene-ring, with formation of chloracetic acids, which Hlasiwetz showed some years since to be the ultimate result of the decomposition. The trichloro-derivative, $C_6Cl_3(OH)_3$, the formation of which thus constitutes the first phase of the reaction, was obtained crystallising with $3H_2O$ in fine needles. In its properties and reactions it is very similar to the well known tribromophloroglucol, and it is to be considered as the corresponding trichloro-derivative. In conclusion the author points out the bearings of his results upon the problems, as yet only partially solved, of the constitutional relationship of the trioxybenzenes and their derivatives, to which he is continuing to devote attention.

33. Note on "The History of Thionyl Chloride." By C. Schorlemmer, F.R.S.

The author in this note refers to certain paragraphs of a recent paper by Dr. Divers (Trans., 1885, 205), relating to the preparation of thionyl chloride.

To the statements contained in that paper the author wishes to add the following:—(1.) Thionyl chloride was first obtained by Hugo Schiff, from Kremer's product (*Annalen*, **102**, 111). (2.) Carius prepared it by heating a mixture of 1 mol. of calcium sulphite and 2 mols. of phosphorus pentachloride, but could not, like Schiff, obtain it quite free from phosphorus oxychloride (*Annalen*, **106**, 328.—(3.) He found that when 3 mols. of calcium sulphite are heated with, not 2, but at least 3 mols. of phosphorus oxychloride, hardly any sulphur dioxide is formed, the product consisting of calcium phosphate and thionyl chloride, which by fractional crystallisation can easily be separated from the excess of oxychloride used (*Annalen*, **106**, 330).

34. "On the Reactions of Selenious Acid with Hydrogen Sulphide and of Sulphurous Acid with Hydrogen Selenide." By E. Divers and T. Shimidzu.

It is true that hydrogen sulphide precipitates from selenious acid under favourable conditions selenium and sulphur in the proportion of one atom of the former to two of the latter, and that hydrogen selenide may precipitate from sulphurous acid, sulphur and selenium in the proportion of one atom of the former to two of the latter; but the physical characters of the precipitates show that these precipitates are mixtures, not compounds. In this communication the authors

state that in precipitating a hot solution of selenious acid, very much sulphur volatilises with the steam.

The authors find that, especially in warm solutions, selenious acid readily oxidises hydrogen sulphide to *sulphuric acid*. It is therefore easy to obtain from a solution of selenious acid a precipitate containing much less than two atoms of sulphur to one of selenium.

Sulphur, they find, instantly decomposes moist hydrogen selenide, forming hydrogen sulphide and selenium. From an excess of sulphur dioxide solution, hydrogen selenide precipitates pure selenium. Hence it is easy to get a precipitate from sulphurous acid containing far more than two atoms of selenium to one of sulphur.

Attention is called to the apparently forgotten experiments of Ditte. He obtained an unstable compound of one atom of selenium to one atom of sulphur, with properties quite distinct from those of a mixture. The authors believe this monosulphide to be the only one of selenium.

The preparation of a monoselenide of iron, almost pure, is described; and from this the authors prepared their hydrogen selenide.

35. "On a New and Simple Method of Quantitative Separation of Tellurium and Selenium." By E. Divers and M. Shimosé.

It has long been known through Rose that the presence of hydrochloric acid is essential to the precipitation of selenium by sulphurous acid. Rose has also pointed out that in presence of dilute sulphuric acid selenium is precipitated by sulphurous acid, but only imperfectly.

The authors show that in presence of comparatively concentrated sulphuric acid the precipitation of selenium is complete by sulphurous acid. They further find that tellurium is not in the least precipitated by sulphurous acid in presence of sulphuric acid unless hydrochloric acid is also present, when its precipitation becomes complete. The application of these facts to the separation of selenium and tellurium is obvious. The mixed substances are heated with concentrated sulphuric acid, which readily oxidises them and for the most part dissolves them. To the acid liquor, sulphur dioxide solution is added until the volume is increased five-fold. This precipitates all selenium. Dilute, and filter; add hydrochloric acid and more sulphur dioxide solution, when the whole of the tellurium will be thrown down. Test analyses are given.

Erratum.—On page 46 of the Abstracts of the Proceedings, line 18, *for* "densities" *read* "boiling points."

NOTICE TO AUTHORS OF PAPERS.

To facilitate the preparation of these "Abstracts of Proceedings," all authors are requested to furnish abstracts of their communications, and to send their papers so that they may be in the hands of the Secretaries, if possible, on the Monday before the day of meeting.

The next Meeting of the Society will be held on Thursday, May 7th, when there will be a ballot for the election of Fellows. (Important.)

The following paper will be read:—

"On the Action of the Copper-Zinc Couple on Organic Bodies (Part X). Benzyl Bromide. By Dr. J. H. Gladstone, F.R.S., and Mr. Tribe.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 8. Session 1884-85.

May 7th, 1885. Dr. Hugo Müller, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. Joseph Fearon Burnett, 23, Alma Square, N.W.; Alfred Daniel Hall, B.A., Baliol College, Oxford; T. Vaughan Hughes, Holywell, N. Wales; Francis George Newbolt, Baliol College, Oxford; Thomas Goddard Nicholson, All Saints' Street, Norwich; Duncan Scott, Macnair, Cliff Edge, Higher Broughton, Manchester; William Hugh Spottiswoode, 4, Grosvenor Place, S.W.; Charles Johnson Taylor, M.A., Toppesfield Rectory, Halstead, Essex; and Robert Wallace, Royal Agricultural College, Cirencester.

The following were elected Fellows of the Society:—

Messrs. F. H. Alcock, M. Cannon, M. Dechan, H. Follows, H. M. Freear, G. H. Gemmell, F. A. Genth, junior, G. M. Gregory, W. B. Hards, E. G. Hogg, C. F. Hope, F. R. Mallet, N. H. J. Miller, A. Milne, T. Muskett, W. H. Reid, R. E. Steel, C. M. Stuart, J. A. Tate and W. P. Wynne.

The following papers were read:—

37. "On some Points in the Composition of Soils; with Results illustrating the Sources of Fertility of Manitoba Prairie Soils." By Sir J. B. Lawes, Bart., LL.D., F.R.S., F.C.S. and J. H. Gilbert, Ph.D., LL.D., F.R.S., V.P.C.S.

This paper is a continuation of one given by the authors at the meeting of the American Association, held at Montreal in the autumn of 1882, entitled "Determinations of Nitrogen in the Soils of some of the Experimental Fields at Rothamsted and the Bearing of the Results on the Question of the Sources of the Nitrogen of our Crops."

The first part of the present paper consists of a *résumé* of the previous one. It was there shown that when crops are grown year after year on the same land without nitrogenous manure, the produce and the yield of nitrogen decline in a very marked degree. This is the case even when a full mineral manure has been applied; and it is the case not only with cereals and with root-crops, but also with *Leguminosæ*. Further, with this great decline in the annual yield of nitrogen of these very various descriptions of plant, when grown without artificial nitrogenous supply, there is also a marked decline in the stock of nitrogen in the soil. Thus, a soil-source of, at any rate, some of the nitrogen of the crops was indicated. Other evidence was also adduced clearly pointing to the same conclusion.

Next, that determinations of the amounts of nitrogen as nitrate in soils of known history as to manuring and cropping, and to a considerable depth, show that the amount of nitrogen in the soil in that form is much less after the growth of a crop than under corresponding conditions without a crop. It was hence concluded that nitrogen had been taken up by the plant as nitrate. In the case of gramineous crops and some others, the evidence points to the conclusion that most, if not the whole, of the nitrogen is so taken up from the soil. It is also clear that some, at any rate, of the nitrogen of *Leguminosæ* has the same source; and the results are in favour of the supposition that in some of the cases the whole of it might be so accounted for. Still it is admitted that, in other cases, this seemed doubtful.

The conditions and the results of a large number of new experiments are next described. It is found that there is very much more nitrogen as nitrate, in soils and subsoils, down to the depth of 108 inches, where leguminous than where gramineous plants have grown. The results point to the conclusion that under the influence of leguminous growth and crop-residue, especially in the case of strong and deep-rooted plants, the conditions are more favourable for the development and distribution of the nitrifying organism; and if this view be confirmed, an important step would be gained towards the more complete explanation of the sources of the nitrogen of the *Leguminosæ*, which assimilate a very large quantity of nitrogen, inducing, as above supposed, the nitrification of the nitrogen of the subsoil, which may thus become the source of the nitrogen of such crops. An alternative obviously is, that the plants might still take up nitrogen from the subsoil, but as organic nitrogen, and not as nitrate. There is, however, no direct experimental evidence in favour of such a view, whilst some physiological considerations, which are discussed, seem to be against it. Again, results show that the soil and subsoil contain less nitrogen as nitrate after the growth of good crops of *Vicia sativa* than where the more shallow-rooted *Trifolium repens* fails to grow.

This is further evidence that the *Leguminosæ* take up nitrogen as nitrate; and in the experiments in question the deficiency of nitric nitrogen in the soil and subsoil of the *Vicia sativa* plots compared with the amount in those of the *Trifolium repens* plot to the depth examined, is sufficient to account for a large proportion of the nitrogen estimated to be contained in the *Vicia* crops.

Other experiments are quoted, which bear less directly on the point, the results of which are, however, accordant; and they at the same time afford illustrations of the loss of nitrogen that the land may sustain by fallow in a wet season, and therefore of the benefits arising from the ground being covered with a crop which takes up the nitrate as it is produced. To conclude on this part of the subject, it may be considered established that much, at any rate, of the nitrogen of crops is derived from the stores within the soil, and that much, and in some cases the whole, of the nitrogen so derived is taken up as nitrates.

This leads the authors to the consideration of the second part of their subject, namely, the sources of fertility of some Manitoba prairie soils.

Soils from Portage la Prairie, from the Saskatchewan district, and from near Fort Ellice, were first examined. They proved to be about twice as rich in nitrogen as the average of arable soils in Great Britain, and perhaps about as rich as the average of the surface soil of permanent pasture land.

Four other Manitoba soils were examined in greater detail. One was from Niverville, 44 miles west of Winnipeg, the second from Brandon, the third from Selkirk, and the fourth from Winnipeg itself. These soils show a very high percentage of nitrogen; that from Niverville nearly twice as high a percentage as in the first 6 or 9 inches of ordinary arable land, and about as high as in the surface soil of pasture land in Great Britain. The soil from Brandon is not so rich as that from Niverville; still the first 12 inches of depth is as rich as the first 6 or 9 inches of good old arable lands. The soil from Selkirk shows an extremely high percentage of nitrogen in the first 12 inches, and in the second 12 inches as high a percentage as in ordinary pasture surface soil. Lastly, both the first and second 12 inches of the soil from Winnipeg are shown to be very rich in nitrogen; richer than the average of old pasture surface soil.

The question arises—how far the nitrogen in these soils is susceptible of nitrification and so of becoming easily available to vegetation. The soils and subsoils were placed in shallow dishes, covered with plates of glass, kept under proper conditions of temperature and moisture for specified periods, extracted from time to time, and the nitric nitrogen determined in the extracts.

The periods were never less than twenty-eight days, and sometimes

more. The rate of nitrification declined after the third and fourth periods. There was a very marked increase in the rate of nitrification in the subsoils during the eighth period compared with the seventh, there having been added only as much as a tenth of a gram of garden soil containing nitrifying organisms. This result is of much interest, affording confirmation of the view that the nitrogen of subsoils is subject to nitrification, if only under suitable conditions, and that the growth of deep-rooted plants may favour nitrification in the lower layers.

Records show that the rich prairie soils of the North-west are competent to yield large crops; but under existing conditions they certainly do not on the average yield amounts at all commensurate with their richness compared with the soils of Great Britain, which have been under arable cultivation for centuries. That the rich prairie soils do not yield more produce than they do, is due partly to climate, but largely to scarcity of labour, and consequent imperfect cultivation, and too luxuriant a growth of weeds; and until mixed agriculture, with stock feeding, can be had recourse to, and local demand arises, the burning of the straw, and deficiency or waste of manure, are more or less inevitable, but still exhausting practices. So long as land is cheap and labour dear some sacrifice of fertility is unavoidable in the process of bringing these virgin soils under profitable cultivation; and the only remedy is to be found in increase of population. Still the fact should not be lost sight of, that such practices of early settlement, however unavoidable, do involve serious loss of fertility.

A table has been prepared showing the comparative characters, as to percentage of nitrogen and carbon, of exhausted arable soils, of newly laid down pasture, and of old pasture soils, at Rothamsted; also of some other old arable soils in Great Britain; of some Illinois and Manitoba prairie soils; and lastly, of some very rich Russian soils. A comparison of the figures leaves no doubt that a rich virgin soil, or a permanent pasture surface soil, is characterised by a relatively high percentage of nitrogen and carbon. On the other hand, soils which have long been under arable culture are much poorer in these respects; whilst arable soils under conditions of known agricultural exhaustion show a very low percentage of nitrogen and carbon, and a low relation of carbon to nitrogen.

In conclusion, the authors said it had been maintained by some that a soil was a laboratory and not a mine; but not only the facts adduced by them in this and former papers, but the history of agriculture throughout the world, so far as it was known, clearly show that a fertile soil is one which had accumulated within it the residue of ages of previous vegetation; and that it became infertile as this residue was exhausted.

38. "Researches on the Relation between the Molecular Structure of Carbon Compounds and their Absorption Spectra." By Professor W. N. Hartley, F.R.S.

In continuation of the author's previous researches (Trans., 1881, 57—60 and 111—128; 1883, 676—678), measurements have been made of the wave-lengths of the rays absorbed by the following substances:—

1. Aromatic hydrocarbons: benzene, the three xylenes and naphthalene.
2. Aromatic tertiary bases and their salts: pyridine, picoline, quinoline and their hydrochlorides.
3. Addition products of tertiary bases and salts: piperidine, tetrahydroquinoline and its hydrochloride.
4. Primary aromatic bases or amido-derivatives and salts thereof: ortho- and para-toluidine and their hydrochlorides.

In the preparation of solutions, a milligram-molecule, that is, the molecular weight in milligrams, was dissolved in 20 c.c. of a diactinic solvent, and made up to a given volume, generally 20 c.c. In this way molecular weights were made to occupy equal volumes. Photographs of the absorption spectra were taken through definite thicknesses of solution. The lines of tin, lead and cadmium were used as references; the positions of the bands were measured on the photographs by means of an ivory rule divided into hundredths of an inch, and those measurements were reduced by means of two curves to oscillation frequencies and wave-lengths. As far as possible, the absorption curves are drawn to a uniform scale. These curves indicate the *molecular actinic absorption* of each substance.

The following deductions are drawn:—

When an atom of nitrogen is substituted for an atom of carbon in the benzene or naphthalene nucleus, the property of selective absorption is still retained.

When the condensation of the carbon and nitrogen in the molecule of a benzenoid compound or tertiary base is modified by the addition of an atom of hydrogen to each atom of carbon and nitrogen, the power of selective absorption is destroyed.

When the condensation of the carbon in quinoline is modified by the combination therewith of four atoms of hydrogen, the intensity of the selective absorption is reduced and is not destroyed.

A very pure specimen of quinoline from coal-tar gave an absorption curve identical with that of quinoline prepared synthetically by Skraup's method. It may further be added that molecular actinic absorption of a salt is different from that of the organic base which it contains, although the acid exerts no absorptive power by itself.

Sometimes the difference is very great, but the area included by the curve of the salt is always less than that of the base. Molecules vibrate as wholes or units, and the fundamental vibrations give rise to secondary vibrations which stand in no obvious relation to the chemical constituents of the molecule, whether these be atoms or smaller molecules. Hence it appears that a molecule is a distinct and individual particle which cannot be truly represented by our usual chemical formulæ, since these only symbolise certain chemical reactions and physical properties, and fail to express any relation between physical and chemical properties.

39. "Researches on the Action of the Copper-zinc Couple on Organic Bodies." Part X. Benzyl Bromide. By Dr. J. H. Gladstone, F.R.S., and Alfred Tribe.

The authors have extended their previous researches on the action of the copper-zinc couple on organic bodies to compounds of the aromatic series. Ortho- and para-bromotoluene are not attacked by the couple, but the isomeric benzyl bromide, C_7H_7Br, is very readily acted upon. So rapid indeed is the action that it is necessary to operate with only very small quantities at a time. Some bromide of zinc is formed, but the main products are bromhydric acid and two apparently different resin-like bodies, the one soluble and the other insoluble in ether, which become viscid at a little above the ordinary temperature, and are decomposed on distillation. Though no specimen was obtained pure, combustions indicated that they were hydrocarbons of the empirical composition C_7H_6, and this was supported by evidence derived from their specific refraction and dispersion. It is proposed to name them α- and β-benzylene. The bromo- and nitro-compounds are uncrystallisable bodies.

In the presence of ether the reaction is very different. The zinc is dissolved in a larger proportion than would be necessary to form $ZnBr_2$; in fact, the proportion of zinc to bromine is very constantly 1 : 1·6. The organic zinc compound was not isolated, but it is decomposed by water with the formation of zinc hydroxide, zinc bromide and toluene. When the compound is strongly heated, dibenzyl also separates from it.

In the presence of absolute alcohol the reaction takes another form. Toluene, C_7H_8, is produced and a bromo-zinc organic compound, doubtless bromoethylate of zinc, $ZnBr.OC_2H_5$. Some dibenzyl was also formed.

In the presence of water the action was slow at the ordinary temperature. The benzyl bromide was found to be mainly resolved into dibenzyl and zinc bromide, but some toluene and zinc oxybromide were also produced.

One or two other compounds formed in smaller quantities were partially examined, but the investigation was not carried further on account of the extremely noxious character of the vapour of the original substance.

40. "On the Selective Alteration of the Constituents of Cast Iron." By Thomas Turner, Assoc. R.S.M.

The paper contains an account of some experiments undertaken with a view of removing manganese from a sample of silicon pig iron containing Silicon, 9·80; Manganese, 1·95; Total carbon, 1·81.

The iron was fused with various substances and the resulting metal analysed. Since manganese is more readily oxidised than iron, it was expected that ferrous silicate would have removed the manganese, leaving the other constituents unchanged. It was found, however, that ferrous silicate produced no alteration in the relative amounts of silicon and manganese present.

Other materials were employed, rich either in silica or oxide of iron, and the author concludes that the active agent in the oxidation of manganese is ferric oxide; that it is not possible by either of the methods employed to remove one constituent without materially altering the amounts of the others present; and that iron of a definite composition may be best obtained by starting with a pure metal and adding the desired constituents.

41. "On the Existence of Nitrous Anhydride in the Gaseous State." By Prof. G. Lunge.

The experiments made by Ramsay and Cundall on this point are not conclusive, as their methods are not free from objections, and the argument based upon the determination of vapour-densities is a very uncertain one in this case. On the other hand, the author has long ago furnished proof of the existence of N_2O_3 as gas, by showing that a vapour possessing that composition is only partially converted into N_2O_4 even when mixed with a tenfold excess of oxygen, and at temperatures ranging between 4° and 150° C. When liquid N_2O_3 evaporates, partial dissociation certainly takes place, but only to a comparatively small extent. This view is also supported by the researches on the vitriol-chamber process, latterly made by the author in conjunction with Naef.

42. "On the Reaction between Nitric Oxide and Oxygen under varying conditions." By Prof. G. Lunge.

Experimental evidence is given for the following conclusions:—

1. That when nitric oxide is mixed in the dry state with an excess of oxygen they combine exclusively, or nearly so, to form N_2O_4.

2. Dry NO and O_2, with an excess of the former, yield a large proportion of N_2O_3 along with N_2O_4, both in the state of gas.

3. In the presence of water, NO in the presence of an excess of O_2 is altogether converted into HNO_3.

4. If NO and O_2 meet in the presence of concentrated sulphuric acid, neither N_2O_4 nor HNO_3 is formed, even with the greatest excess of oxygen; but the reaction is—

$$4SO_4H_2 + 4NO + O_2 = 4SO_2(OH)(ONO) + 2H_2O.$$

The bearing of these facts on the theory of the vitriol-chamber process is then discussed. The author considers that N_2O_3, and not NO as hitherto assumed, is the carrier of oxygen, and that as long as any appreciable quantity of SO_2 is present, no nitric oxide is formed, the following being the reactions whereby the sulphuric acid is formed:—

$$2SO_2 + N_2O_3 + O_2 + H_2O = 2SO_2(OH)(O_2N)$$
$$2SO_2(OH)(O_2N) + H_2O = 2SO_2(OH)_2 + N_2O_3.$$

Discussion.

Dr. Armstrong said that he had always been of opinion that Prof. Lunge's experiments could not be accepted as establishing the existence of N_2O_3 as gas. The fact that NO acts upon nitric acid in presence of sulphuric acid, reducing it to the nitrous state, vitiates the results in those cases in which the gases were passed into sulphuric acid, the amount of nitric and nitrous nitrogen in the solutions thus obtained being then determined. Lunge admits that NO does so act, and yet continues to employ the method. It is unimportant whether or no the action be readily effected to the full extent; if such an action take place at all, the method is necessarily faulty, and therefore inapplicable to the differentiation of mixtures of N_2O_4 with NO from N_2O_3. Lunge's experiments described in *Dingl. polyt. J.*, **233**, 68, are not only subject to this criticism, but it is also probable that with the arrangement he employed the gases never became thoroughly mixed; on passing NO and air through a similar apparatus, Dr. Armstrong had found this actually to be the case. Lunge and Naef's observations on the composition of the chamber gases were a complete riddle to him. It appeared almost incredible that the oxidised nitrogen could exist entirely as N_2O_3, in presence of a large excess of oxygen, SO_2 and NO being absent. Experiments on the behaviour of NO towards oxygen in presence of third bodies, however valuable in themselves, could not be accepted as throwing any light on the question at issue.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Third Annual Report of the United States Geological Survey; 4to. Washington, 1883; from the Director.

Report of the Director of the Mint on the Production of Precious Metals in the United States in 1883; Washington, 1884: from the Director.

Report of the United States National Board of Health for 1882; Washington, 1883: from the Director.

Geology of the Comstock Lode and the Washoe District (Monographs of the U.S. Geological Survey, vol. III). By G. F. Becker. 4to.

Atlas to same. Large folio. Washington, 1882: from the Director.

Elementary Nitrogen and the Synthesis of Ammonia. By G. S. Johnson; London, 1885: from the Author.

Familiar Lessons on Food and Nutrition. By T. Twining; London, 1882: from the Author.

II. *By Purchase.*

Anleitung zur Qualitaliven Chemischen Analyse. Von C. R. Fresenius; 15te auflage, 1ste abth: Braunschweig, 1885.

Graham-Otto's Ausführliches Lehrbuch der Chemie, Erster Band. 1ste Abth. Physikalischer Lehren. Von A. Winkelmann: Braunschweig, 1885.

Documents sur les Falsifications des Matières Alimentaires, et sur les Travaux du Laboratoire Municipal. 2me Rapport. 4to. Paris, 1885.

Titles of Papers of interest to Chemists recently read before Societies in the United Kingdom:—

"On the Fibrin-yielding Constituents of the Blood." By Dr. Wooldridge.

"The Essential Nature of the Colouring of Phytophagous Larvæ (and their Pupæ); with an Account of some Experiments upon the relation between the Colour of such Larvæ and that of their Food-plants." By E. B. Poulton.

"Further Observations on Enterochlorophyll and Allied Pigments." By Dr. C. A. MacNunn.

"A Study of the Thermal Properties of Ethyl Alcohol." By Dr. W. Ramsay and Dr. Sidney Young.

"On the Solubility of Calcium Sulphate in Water in the presence of Chlorides." By Prof. Tilden, F.R.S., and W. A. Shenstone.

"Contributions to the Chemistry of Chlorophyll." By E. Schunck, F.R.S.

"On the Electric Resistance of a New Alloy named Platinoid." By J. T. Bottomley.

Royal Society of London, April 16th, 23rd, 30th; May 7th.

"On Chlorophyll from the Deep Sea." By Prof. W. N. Hartley, F.R.S.

"On Papers by Messrs. Haas, Clève and Lecoq de Boisbaudran, on the Production of Peroxides by means of Peroxide of Hydrogen." By J. Gibson, Esq., Ph.D.

"On Supersaturation." By W. W. J. Nicol, Esq.

Royal Society of Edinburgh, April 6th.

"Address of Dr. Percy, F.R.S., the President of the Iron and Steel Institute."

"On the Blast Furnace Value of Coke from which the Products of Distillation have been Collected." By Mr. I. Lowthian Bell, F.R.S.

"On more Recent Results obtained with the Simon-Carvés Coke Ovens, especially as regards Coal Tar." By Mr. Watson Smith.

"On the Simon-Carvés Coking Process." By Mr. Henry Simon.

"Note with Reference to the Methods proposed for Coking Coal and recovering Volatile Matter." By Prof. Armstrong.

"The Properties of Malleable Iron deduced from its Microscopic Structure." By Dr. H. Wedding.

"On the Microscopic Structure of Steel." By Dr. Sorby, F.R.S.

"On Natural Gas, and its Utilisation for Manufacturing Purposes in the United States." By Mr. A. Carnegie, New York, U.S.A.

"On a Modified Type of the Siemens Gas-producer, whereby the Gases are Enriched and the Bye-products Recovered." By Mr. J. Head.

Iron and Steel Institute, May 6th, 7th, 8th.

"On the Conversion of Heat into Useful Work. (4th Lecture.) By W. Anderson.

"The Chemistry of Ensilage." By F. J. Lloyd.

"Researches on Silk Fibre." By T. Wardle.

Journal of the Society of Arts, May 1st.

At the next Meeting, on May 21st, the following papers will be read:—

"Spectroscopic Observations on dissolved Cobaltous Chloride." By Dr. W. J. Russell.

"Colorimetric Method for the Estimation of Iron." By Andrew Thomson.

"Some Sulphur Compounds of Calcium." By V. H. Veley.

Dr. Klein is unfortunately unable to deliver his promised Lecture.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 9. Session 1884–85.

May 21st, 1885. Dr. Hugo Müller, F.R.S., President, in the Chair.

Messrs. E. G. Amphlett and E. G. Hogg were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Thomas Cradock Hepworth, 32, Cantlowes Road, Camden Square, N.W.; Leonard de Koningh, 40, Methley Street, S.E.; Charles Langer, 43, Burton Crescent, W.C.; James Sharp, The Towers, Low Moor, near Bradford; James Pender Smith, 12, Bromley Road, Lee, S.E.

The following papers were read:—

43. "A Colorimetric Method for Determining small Quantities of Iron." By Andrew Thomson, M.A., B.Sc.

The author has applied the well-known thiocyanate reaction of ferric salts to the quantitative determination of small quantities of iron. The method is almost universally applicable, silver and copper, and in some cases cobalt, being the only common metals that interfere. To perform the analysis, a weighed quantity of substance is dissolved in acid, the excess of acid driven off by evaporation, the iron, if necessary, converted into ferric salt by means of potassium permanganate, and finally the solution is diluted to 1 litre. Into each of two similar cylinders, 5 c.c. of dilute chlorhydric or nitric acid (1 : 5), and 15 c.c. of potassium thiocyanate solution (containing 40 grams per litre) are poured, and to one a measured bulk of the solution to be tested is added; both cylinders having been filled up to the same height with distilled water, a standard solution of ferric salt containing 0·0001 gram Fe per c.c. is added to the other cylinder in quantity sufficient to produce a colour matching that in the cylinder containing the substance under examination.

Discussion.

Dr. Percy Frankland said that he had been in the habit for several years past of using such a method to determine minute amounts of iron in water.

Prof. Clowes remarked that it would be important to employ a constant amount of acid, and that the presence of mercuric chloride was especially to be avoided.

44. "On some Sulphur Compounds of Calcium." By V. H. Veley.

To prepare calcium sulphide in the dry way, pure calcium oxide, hydrated in an atmosphere free from carbonic anhydride, was introduced into a suitable apparatus and heated in a current of hydrogen sulphide at a temperature of 80°, the water eliminated in the course of the change being collected in a drying tube. Starting with known weights of calcium hydroxide, known weights of water and of calcium sulphide retaining a small proportion of water were obtained, and on adding the latter quantity as determined by analysis to the former quantity collected in the drying tube, it was found that the reaction expressed in the equation $Ca(OH)_2 + H_2S = CaS + 2H_2O$ was practically realised.

It was observed that *dry* calcium oxide is not acted upon by *dry* hydrogen sulphide, and thus another instance is presented of the inability of two substances or elements to directly combine or react without the intervention of a third substance or element.

Anhydrous calcium sulphide is a white powder when freshly prepared, but quickly turns yellow from the formation of oxidised products.

To prepare calcium hydrosulphide in the wet way, known weights of calcium oxide were added to known weights of water saturated with hydrogen sulphide at ordinary temperature, and a current of the gas passed through the liquid until the calcium oxide was dissolved; the water evaporated by the passage of the gas was collected in a drying tube. The gain in weight of the solution, together with the collected water, less the known weights of calcium oxide, gives the weight of hydrogen sulphide absorbed. The atomic ratio of calcium to sulphur in the resultant solution was determined. It was found that for solutions not containing more than 25 per cent. of calcium hydrosulphide (reckoned as anhydrous) the reaction which took place is represented by the equation $CaO + 2H_2S = Ca(SH)_2 + H_2O$.

Calcium sulphocarbonate was prepared by passing hydrogen saturated with the vapour of carbon disulphide into water in which calcium sulphide was suspended. A red solution was produced, the

properties of which accorded with those noticed by Berzelius. From this a red crystalline material separated on evaporation, approximately represented by the formula $Ca(OH)_2CaCS_3,7OH_2$.

Dry calcium sulphide does not absorb carbon disulphide, and it is essential to add relatively large quantities of water to ensure the absorption. When a solution of calcium hydrosulphide is submitted to a current of hydrogen saturated with the vapour of carbon disulphide, hydrogen sulphide is at first given off with precipitation of calcium hydroxyhydrosulphide, HS·Ca·OH; the absorption of carbon disulphide commences only when the precipitation of this last substance is practically completed. Calcium hydroxyhydrosulphide is presumably the absorbent of carbon disulphide in the material prepared in the gasworks by passing coal-gas contaminated with hydrogen sulphide into slaked lime.

45. "Spectroscopic Observations on Dissolved Cobaltous Chloride." By Dr. W. J. Russell, F.R.S.

The characteristic absorption-spectrum given by cobaltous chloride after dissolution in such media as pure and dry potassium chloride, sodium chloride, calcium chloride, alcohol, glacial acetic acid and in chlorhydric acid, is seen also in an aqueous solution. Hydrated cobaltous chloride gives an entirely different spectrum. If a somewhat faint indication of the spectrum of the chloride be taken as a standard, it is found possible to determine with tolerable accuracy when the amount of anhydrous chloride in solutions of varying strength and temperature is identical with that in the standard solution. A solution containing 4·18 grams of cobalt chloride in 10 c.c. of water at 0° C., when observed through a thickness of 7 mm., forms a convenient standard. If to 10 c.c. of such a solution 2·9 c.c. of water be added, then on raising the temperature to 33°, an amount of anhydrous chloride is re-formed identical with that existing in the standard solution at 0°: this rise of temperature exactly counteracts the effect of adding 2·9 c.c. of water. A series of determinations were made in this manner, and it was found that the number of c.c. of water added to the 10 c.c. of standard being as given in the upper line, the temperature at which the spectrum appeared was as given in the lower line in the table :—

2·1		2·9		4·3		7·4		8·9	
26°		33°		43°		55°		63°	
	10·3		12·1		15·0		16·0		
	70°		75°		87°		95°		

Again, taking the most dilute solution, in which 16 c.c. of water

had been added to 10 c.c. of the standard solution, it was found that the same change was effected, *i.e.*, that the chloride spectrum could be developed in it, by the addition to the solution of either 0·864 gram of hydrogen chloride gas, or 5·26 of sulphuric acid, or 2·47 of calcium chloride; but that the addition of sodium chloride would not develop the bands, although on heating the solution after saturating it with this salt a temperature of 34·5° was sufficient, instead of 95°, to develop the bands.

Zinc chloride was found to act in a different manner. Notwithstanding its power of combining with water, on adding it to the cobalt solution no banded spectrum shows itself, and even when added to a solution in which the spectrum is visible, it causes its disappearance. The explanation is that it must have combined with cobalt chloride, forming a new and stable compound. On evaporating the solution this was found to be the case, and a new salt, a compound of cobalt and zinc, crystallised out. Cobalt bromide, both as a solid and in solution, gives a spectrum very similar to that given by the chloride, but the corresponding bands are nearer the red end of the spectrum. The salt is far more soluble in water than the chloride, and has a stronger affinity for water, as is shown by the much higher temperature required to neutralise the power with which water combines with it. The following determinations similar to those made with the chloride show the increase of temperature necessary to counteract the combining power of given quantities of water with cobalt bromide:—

Standard + Water.	Temp.
10 c.c.	0° C.
10 „ + 3·0	51
10 „ + 4·3	57
10 „ + 7·4	91

Discussion.

Captain Abney said experience had taught him that it was necessary to be guarded in drawing conclusions as to changes in molecular composition from observations of spectra; the pitfalls were very numerous. He did not think it safe to conclude that a double salt was not formed because no change in the spectrum was observed when the substance added is itself non-absorbent, as is the case with potassium or sodium chloride.

Mr. Friswell had noticed a somewhat similar case when working as Mr. Lockyer's assistant. Whereas an aqueous solution of iodine produces general absorption, a solution in concentrated sulphuric acid or in carbon bisulphide has a spectrum very similar to that of iodine vapour. In the one case there appeared to be some combination; in the other a mere entanglement of the iodine by the solvent.

Captain Abney asked if Mr. Friswell had noticed a linear spectrum in the case of the sulphuric acid or bisulphide solution. Mr. Lockyer had told him that it was linear, but he had entirely failed to discover such a spectrum. Mr. Friswell replied that to the best of his recollection it was but a rough approximation to a linear spectrum.

Prof. McLeod remarked that Dr. Russell's observations appeared to indicate a sudden change on diluting the solution or altering its temperature; it was scarcely probable, however, that there would be an abrupt passage from the hydrated to the anhydrous condition.

Dr. Armstrong inquired if it were not possible that changes might be discovered to have taken place on extending the observations to other regions of the spectrum beyond the ordinarily visible portions?

Mr. Veley remarked that the argument was inconclusive which was based on the observation that a double salt was obtained on evaporating the mixed solutions of cobalt and zinc chlorides, and not when sodium or potassium chloride was present instead of zinc chloride, as cases were known in which bodies existing in solution were decomposed as the liquid was evaporated off.

Mr. Cross asked if Dr. Russell had made any experiments as to the effect produced by adding colloids.

Dr. Morley thought it not impossible that the anhydrous chloride should exist in solution. It was known that a concentrated solution of potassium hydroxide decomposed silver chloride, the reverse change taking place in dilute solution; the former change had been explained on thermochemical principles as due to the presence of anhydrous hydroxide.

Mr. Pickering said that if anhydrous cobaltous chloride could exist in solution, it must be an exception, no similar case being known.

Dr. Russell, in reply, said that he had desired to bring forward suggestions rather than definite conclusions. His reason for assuming the existence of the anhydrous chloride in aqueous solution was that it was possible to obtain the same spectrum as when the chloride was dissolved in many different and distinct media, for instance in fused potassium chloride, in glacial acetic acid, or in anhydrous alcohol. He had been informed by Captain Abney that the "cobalt-tune" was played in the visible spectrum, otherwise he would not venture to lay such stress on his observations. In answer to Professor McLeod's observations, he pointed out that the change *was* gradual, not sudden as he appeared to think.

46. "The Sulphides of Titanium." By Prof. T. E. Thorpe, F.R.S.

No action takes place on passing a mixture of hydrogen sulphide and carbon disulphide vapour, *both carefully dried*, over titanic oxide, TiO_2, at the highest temperature of a Fletcher's tube-furnace; but

when no pains are taken to dry the sulphides, the oxide is converted into the hitherto unknown *titanium sesquisulphide*, Ti_2S_3. Thus prepared it is a greenish-black powder. The monosulphide, TiS, is obtained on heating this sesquisulphide in dry hydrogen. The complete series of corresponding oxides and sulphides of titanium is therefore now known.

47. "Note on the Formation of Titanous Chloride." By Prof. T. E. Thorpe, F.R.S.

If a quantity of mercury and titanium tetrachloride are sealed up in a tube together and briskly shaken, so as to throw the mercury into extremely fine globules, it will be noticed after a short time that a violet crystalline powder is gradually formed, and after some days the contents of the tube appear to be no longer liquid. The tetrachloride is, in fact, gradually converted, even at the ordinary temperature of the air, into the violet titanous chloride by the action of the finely divided mercury, with the simultaneous formation of calomel. The conversion is more rapidly accomplished by placing the tube in a water-bath; at a temperature of about 98° the contents of the tube seem to become solid in about half an hour. If the temperature of the tube be now raised to about 200—250° the reverse change occurs; titanium tetrachloride and metallic mercury are reformed.

This alternate formation of the solid violet trichloride and the colourless liquid tetrachloride in contact with mercury or calomel, may be repeated an indefinite number of times, and constitutes an interesting example of the mode in which the direction of a chemical change is modified by temperature.

Friedel and Guérin (*Ann. Chim. Phys.* [5], **7**, 24) obtained the violet chloride by the action of molecular silver on the tetrachloride but in this case a temperature of 200° is required to bring about the change. At a still higher temperature the reverse action occurs, as in the case with mercury.

RESEARCH FUND.

A meeting of the Research Fund Committee will be held in June. Fellows desiring grants are requested to make application before June 11th.

At the next Meeting, on June 4th, the following paper will be read:—

"On the Constitution of the Haloid Derivatives of Naphthalene." By Prof. Meldola.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 10. Session 1884–85.

June 4th, 1885. Dr. Hugo Müller, F.R.S., President, in the Chair.

Mr. Harold Follows was formally admitted as a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Gibson Dyson, 231, Wilton Terrace, Manchester; William Herbert Hyatt, 9, Margravine Gardens, West Kensington, W.; Gerald Martin, Imperial Mint, Bombay; Thomas J. Menzies, M.A., 211, Crown Street, Glasgow; John Dominie Vieira, Rio de Janeiro; Herman J. Vueté, 79E, 111th Street, New York; Arthur Benjamin Winstone, 53, Russell Square, W.C.; T. G. Wormley, Philadelphia; James C. Wright, 14, Hill Street, Irvine, N.B.

The following were elected Fellows of the Society:—Messrs. Joseph Fearon Burnett, Thomas J. Greenway, Alfred Daniel Hall, T. Vaughan Hughes, Duncan Scott Macnair, Francis George Newbold, Thomas Goddard Nicholson, William Hugh Spottiswoode, Charles Johnson Taylor, Robert Wallace.

The following paper was read:—

48. "On the Constitution of the Haloïd Derivatives of Naphthalene." By Prof. Meldola.

The starting point of the present research is a new bromonitro-α-acenaphthalide (m. p. 225°) obtained by adding bromine to a cold acetic acid solution of Liebermann's mixture of nitracenaphthalides: under these circumstances the paranitracenaphthalide is alone attacked. The bromonitracenaphthalide thus produced furnishes a new bromonitronaphthylamine on hydrolysis (m. p. 127°; $NH_2 : Br : NO_2 = 1 : 2 : 4$), and by the action of aqueous caustic alkalis it is converted

into a corresponding bromonitronaphthol (m. p. 146°), of which several metallic derivatives have been prepared and analysed.

The author has incidentally prepared Liebermann's γ-nitracenaphthalide in a state of purity: it melts at 187°. All the derivatives which have hitherto been obtained from it are identical with those produced from paranitracenaphthalide, and it is not improbable that the γ-modification is a physical isomeride of the para-compound; the author finds, however, that the γ-compound is less readily acted upon by bromine than ordinary paranitracenaphthalide.

The constitution of Liebermann's nitrobromonaphthylamine (from bromacenaphthalide) has been established by reducing its acetyl-derivative, which is found to yield an "anhydro-base."

Two nitrobromonaphthalenes have been prepared from the two nitrobromonaphthylamines (Liebermann's and the author's); they do not differ in appearance or melting point (131—132°), although from the manner in which they are formed it must be concluded that in the one $NO_2 : Br = 2 : 4$, and that in the other $Br : NO_2 = 2 : 4$, a view which is confirmed by the fact that both furnish the same meta-dibromonaphthalene (m. p. 64°) when the NO_2-radicle is displaced by bromine.

These two nitrobromonaphthalenes are readily reduced by adding zinc-dust to a solution in cold acetic acid. The resulting bromonaphthylamine in which $NH_2 : Br = 2 : 4$ melts at 71·5°, and that in which $Br : NH_2 = 2 : 4$ melts at 62°; their acetyl-derivatives have practically the same melting point, viz., 186·5—187°.

Another atom of bromine is readily introduced into each of these bromacenaphthalides, but in both cases enters the "unsubstituted benzene-ring," taking up an α-position in that in which the acetamido-group is in the α-position, and a β-position in that in which the NH.$\overline{Ac}$-group is in the β-position. The dibromacenaphthalides melt at about the same temperature (221—222°); the corresponding dibromonaphthylamines melt respectively at 101—102° (the α-NH_2 mod.) and 105° (the β-NH_2 mod.), and both furnish the same dibromonaphthalene (m. p. 74°), when the NH_2-radicle is displaced by hydrogen. There are two formulæ possible for each modification which are compatible with the facts, but the more probable formulæ of the dibromonaphthylamines are, according to the author—

$$NH_2 : Br : Br = 1 : 3-1' \text{ (m. p. 101—102°)}$$
$$NH_2 : Br : Br = 2 : 4-2' \text{ (m. p. 105°)},$$

the constitution of the dibromonaphthalene from them being probably $Br : Br = 1 - 3'$.

The tribromonaphthalenes corresponding to the two dibromonaphthylamines have been prepared, and probably contain the bro-

mine-atoms in the relative positions 1 : 3 — 1′ (m. p. 105°), and 2 : 4 — 2′ (m. p. 110°).

The next part of the paper deals with the iodine-derivatives of naphthalene, of which the two moniodonaphthalenes have up to the present time been the sole representatives. The mixture of nitracenaphthalides obtained by nitrating a solution of α-acenaphthalide in acetic acid was converted by the action of alcoholic potash into a mixture of the corresponding nitronaphthylamines; the latter were then diazotised and converted into the corresponding nitroiodonaphthalenes by the action of iodhydric acid. By fractional crystallisation from alcohol, two modifications were isolated in a state of purity, the chief product being the para-modification (α-nitriodonaphthalene, $I : NO_2 = 1 : 4$, m. p. 123°), and the other the ortho-compound (β-nitriodonaphthalene, $I : NO_2 = 1 : 2$, m. p. 108·5°). A third (γ) nitriodonaphthalene ($NO_2 : I = 1 : 2$, m. p. 88·5°) has been obtained by hydrolysing Jacobsen's nitracenaphthalide (*Ber.*, **14**, 805) and displacing the NH_2-group by iodine as before.

β-Nitriodonaphthalene cannot be reduced without the iodine-atom becoming displaced, and it then furnishes β-naphthylamine. The α- and γ-modifications can be converted by reduction with zinc-dust in cold acetic acid solution into the corresponding iodonaphthylamines, but owing to their instability these bases have not yet been isolated. By immediately diazotising and decomposing with hydriodic acid, however, the two iodonaphthylamines may be converted into the corresponding di-iodonaphthalenes; the 1 : 4 modification melts at 109—110°, and the 1 : 2 di-iodonaphthalene melts at 81°.

By displacing the NH_2-group in the bromonaphthylamines by iodine, three bromiodonaphthalenes have been obtained, viz., $Br : I = 1 : 4$ (m. p. 83·5°), $Br : I = 1 : 2$ (m. p. 94°), and $Br : I = 1 : 3$ (m. p. 68°).

Neither α- nor β-acenaphthalide can be directly iodised, but α-iodacenaphthalide (m. p. 196°) has been prepared by reducing α-nitroiodonaphthalene (m. p. 123°) and acetylating the product by cohobation with acetic anhydride. This iodacenaphthalide (m. p. 235—236°) furnishes a nitro-compound which is converted by the action of caustic potash into nitriodonaphthol, $HO : NO_2 : I = 1 : 2 : 4$, m. p. 145—146°.

Iodobetanaphthol has been prepared by treating a solution of betanaphthol in glacial acetic acid with iodine in the presence of lead acetate, and anhydrous sodium acetate dissolved in the same solution. It crystallises in white needles melting at 97°, and is soluble in very dilute alkalis.

Discussion.

Dr. Armstrong said that it was not only in passing from the di- to the tri-derivatives of naphthalene that the law of substitution was no longer the same as for benzene derivatives; the beta-mono-derivatives of naphthalene exhibited marked peculiarities, attack being as a rule shifted "to the other ring" whenever a negative radicle was present in the β-position, as in the case of betanaphthol, for example. This was also observed in the formation of disulphonic acids from naphthalene. In these cases it was probable that the radicle took up such a position in the previously unoccupied "ring" that the compound having what might be regarded as the more symmetrical of the two possible symmetrical formulæ was produced; on this account, he was inclined to take the opposite view to Prof. Meldola regarding the formulæ of the dibromonaphthylamines.

Mr. Groves remarked that Prof. Meldola had, he thought, introduced a great improvement in the method of iodising by operating in presence of a lead salt. The use of mercuric oxide was objectionable on account of the solubility of mercuric iodide in almost everything; it was, in fact, only possible to get rid of it by displacing the mercury by some other metal.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

A Treatise on Practical Chemistry and Qualitative Inorganic Analysis; by F. Clowes, 4th Ed., London, 1885: from the Author.

The International Scientist's Directory; compiled by S. E. Cassino; Boston, U.S.A., 1885: from E. C. Conrad, Esq.

Destructive Distillation; by E. J. Mills, 2nd Edition, London, 1883: from E. C. Conrad, Esq.

Manual of Chemistry; by W. Simon, London, 1885: from the Publishers, Messrs. Baillière, Tindall, and Cox.

The Structure of the Wool Fibre in its Relation to the Use of Wool for Technical Purposes; by F. H. Bowman, Manchester, 1885: from the Author.

Fresenius' Quantitative Analysis; translated by C. E. Groves, Vol. II, Part 1, London, 1885: from the Translator.

Sept Études sur 1, L'état sphéroïdal; 2, Les explosions des machines à vapeur; 3, Les trombes; 4, La grêle; 5, L'électricité atmosphérique; 6, La réfraction latérale; 7, L'adhésion entre les liquides et les solides: par J. Luvini, Turin, 1884: from the Author.

The Theory and Practice of Sweet Ensilage; by G. Fry, London, 1885: from the Author.

Report of the 54th Meeting of the British Association for the Advancement of Science, held at Montreal in August and September, 1884; London, 1885: from the Association.

Familiar Lessons on Food Nutrition; a Handbook to the Food Department of the Parkes' Museum of Hygiene: by T. Twining, London, 1882.

II. *By Purchase.*

Physikalische Krystallographie: von P. Groth, Leipzig, 1885.

Traité de Minéralogie, appliqué aux Arts: par R. Jagnaux.

Titles of papers of interest to chemists recently read before Societies in the United Kingdom:—

"The Solar Spectrum from λ7,150 to λ10,000." By Capt. Abney, R.E., F.R.S. Royal Society of London, May 21st.

"Effect of Pressure on the Temperature of Minimum Compressibility of Water." By Prof. Tait.

"Note on the Variation by Pressure of the Melting Point of Paraffin, &c." By W. Peddie.

"Note on the Thermal Effects of Tension on Water." By E. N. Stewart.

"On the Temperature of the Water in the Firth of Forth." By H. R. Mill, B.Sc.

"On the Volume of Mixed Liquids." By R. Brown.

"On the Visual Grating and Glass-lens Solar Spectrum, as observed in 1884." By Prof. Piazzi Smyth.

"On the Chemistry of Japanese Lacquer." By Hikorokuro Yoshida.

Royal Society of Edinburgh, April 20th, May 18th, June 1st.

"Development of Liquid Fuel for Marine Purposes." By Vice-Admiral J. H. Selwyn. United Service Institute, May 8th.

"The American Oil and Gas Fields." By Prof. Dewar, F.R.S. Society of Arts, May 20th.

NOTICE TO FELLOWS.

Library.—The Library will be closed in the evening during July and September, and entirely during August for the re-arrangement of the books. Fellows are requested to return all books not later than July 31st.

Journal of the Chemical Society (Abstracts).—A title-page has been issued with the June number of the Journal for the convenience of those who find it inconvenient to bind the "Abstracts" in a single volume. The "Abstracts" will, however, be paged continuously, and two title-pages will be issued at the close of the year, so that those who prefer to do so may bind the "Abstracts" in a single volume.

At the next Meeting, on June 18th, the following papers will be read :—

"The Decomposition and Genesis of Hydrocarbons at High Temperatures. The Products of the Manufacture of Gas from Petroleum." By Drs. Armstrong and A. K. Miller.

"The Non-Crystallisable Products of the Action of Diastase upon Starch." By Horace T. Brown and G. H. Morris, Ph.D.

"On the Decomposition of CO_2 at High Temperatures." By H. B. Dixon.

"On the Influence of Silicon upon the Properties of Cast Iron." By T. Turner.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 11. Session 1884-85.

June 18th, 1885. Dr. Hugo Müller, F.R.S., President, in the Chair.

Messrs. Jos. F. Burnett and Harry M. Freear were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. William James Bell, M.A., The Manor House, Highbury, N.; Albert Ivatt, 1, Ching Villas, Mill Road, Cambridge; Edward de Souza, Rangoon; Ernest William Wiltshire, 25, Granville Park, Lewisham.

The following gentlemen were duly elected Fellows of the Society:—Messrs. Harry Haslett; Thomas Cradock Hepworth; Leonard de Koningh; Charles Langer; Arthur Richardson; James Sharp; James Pender Smith; James Spilsbury.

The following papers were read:—

49. "On the Decomposition and Genesis of Hydrocarbons at High Temperatures. I. The Products of the Manufacture of Gas from Petroleum." By Henry E. Armstrong and A. K. Miller, Ph.D.

Having carried the examination of the various products of the decomposition of petroleum effected at high temperatures, in the manufacture of oil-gas (see paper in the *Journal of the Society of Chemical Industry*, September, 1884), as far as can usefully be done with the material originally dealt with, the authors now describe their methods and results; they remark, however, that these must be regarded as little more than preliminary, and that it will be necessary to repeat the investigation on a much larger scale, and to introduce new and improved methods. The products examined are (1) the portion of the compressed gas which combines with bromine; (2) the liquid deposited during compression of the gas to about ten atmospheres; (3) the portion of the tar which is volatile in steam.

1. By far the chief constituents of the mixture of bromides obtained by scrubbing the compressed gas by bromine are ethylene bromide and crotonylene tetrabromide, $C_4H_6Br_4$; propylene and butylene bromides have also been separated from it. The gas is practically free from hydrocarbons of the acetylene series capable of producing a precipitate in an ammoniacal cuprous solution.

2. The liquid deposited during compression of the gas is a complex mixture of olefines, of hydrocarbons of the C_nH_{2n-2} series, and of benzenes. The presence in it of *normal* amylene, hexylene and heptylene has been demonstrated by the study of the products of oxidation of the various fractions. It is saturated with crotonylene, and contains a considerable quantity of the next homologue, C_5H_8; this latter hydrocarbon has not been previously described: it boils at 45°, and yields a tetrabromide which crystallises from alcohol in long flat prisms melting at 114°. All attempts to separate a hydrocarbon having the properties of Schorlemmer's hexoylene from the fraction boiling at 80—82°, have hitherto been unsuccessful, the statement previously made by one of the authors that this hydrocarbon was present having been based on determinations which have since been discovered to be faulty. The liquid deposited during compression of oil-gas is rich in benzene and toluene, but contains only traces of higher benzenes.

3. The steam distillate from the tar contains the less volatile hydrocarbons present in the liquid deposited during compression of the gas together with a great variety of others. It is rich in hydrocarbons which are readily polymerised by sulphuric acid; these appear to be mainly members of the C_nH_{2n-2} series, such as Schorlemmer discovered in the light oils from cannel and boghead coal, and which yield no acid higher than acetic on oxidation. The three xylenes and mesitylene and pseudocumene are present in about the same relative proportions as in ordinary coal-tar; but in addition, the oil-gas tar contains certainly one—probably two—*higher* member of the benzene series: the amount obtained has not been sufficient, however, to permit of the precise determination of its nature. A very considerable amount of naphthalene may be separated from the tar; benzenoid hydrocarbons of higher boiling point than naphthalene have also been obtained in small quantity. A certain, although relatively small, amount of a complex mixture of saturated hydrocarbons has also been separated from the tar: the quantity of material at their disposal has not enabled the authors to separate these to their satisfaction, and in a state sufficiently approaching purity: they are inclined to believe, however, that the mixture does not consist of paraffins, but of hydrocarbons of the C_nH_{2n} series—such as form the chief constituents of Russian petroleum.

The hydrocarbons mentioned are by no means the sole constituents of the material examined, but merely those which have been proved to be present.

The theoretical conclusions to be deduced from the results are in some respects interesting. It would appear that *only normal* olefines are present, and it is also remarkable that apparently this series is not represented by terms higher than heptylene. No true acetylenes have been detected; the crotonylene obtained is either *methylallene*, $CH_3{\cdot}CH{\cdot}C{\cdot}CH_2$, or *dimethylene-ethane*, $C_2H_2(CH_2)_2$, and from their behaviour on oxidation it is probable that the homologous hydrocarbons are closely related to it. Hence it may be inferred that in the formation of hydrocarbons of the C_nH_{2n-2} series at high temperatures from normal olefines of the formula $C_nH_{2n+1}{\cdot}CH{\cdot}CH_2$ two atoms of hydrogen are removed in such a way that the terminal $CH_3{\cdot}CH_2$ radicle in the formula becomes either $CH_3{\cdot}CH$ or $CH_2{\cdot}CH$; although the production of acetic acid on oxidation of the hydrocarbons favours the former hypothesis, it is not safe to accept it until several of the hydrocarbons of the C_nH_{2n-2} series have been isolated and more completely studied. The possibility that *saturated* hydrocarbons of the C_nH_{2n} series are among the products is especially noteworthy, although it must not be forgotten that such hydrocarbons might have been original constituents of the petroleum used in making gas.

To settle this and other questions, it is proposed to prepare oil-gas from *solid* paraffin on a sufficient scale to obtain the quantity of material required for the investigation.

50. "On the Non-crystallisable Products of the Action of Diastase upon Starch." By Horace T. Brown and G. H. Morris, Ph.D.

The authors first show that the previous work of one of them (Brown and Heron, Trans., 1879, 596) confirmed O'Sullivan's statement that when starch is transformed by diastase, the optical behaviour and cupric reducing power of the mixed products are such as would be accounted for by the presence only of *maltose* and a non-reducing *dextrin* having a rotatory power of $[\alpha]_{j3{\cdot}s6}216°$.

They then proceed to show that by fractionating the starch products with alcohol all the several fractions agree in giving results which can also be interpreted in terms of maltose and dextrin only; and they thus establish a criterion of purity for any portion of the starch products which can be separated, ascribing the results of other observers, where they do not conform to this rule, either to the presence of impurities or to errors of determination.

The tendency of the mixed products from any starch transformation when subsequently acted upon by malt extract at 50—60° is rapidly

to attain a state of equilibrium, which is represented by the equation No. 8 of the series of Brown and Heron—

$$10'C_{12}H_{20}O_{10} + 8H_2O = 8C_{12}H_{22}O_{11} + 2C_{12}H_{20}O_{10}.$$
Starch. Maltose. Dextrin.

The mixed products of the transformation then have a specific rotatory power of $[\alpha]_{j3\cdot s6}162{\cdot}6°$, and a cupric reducing power of $_{s3\cdot s6}$ 49·3, the percentage composition being maltose 80·9, dextrin 19·1.

The rapid degradation of all the higher transformations down to this point is due to the hydrolysis of the more complex polymeric dextrins to dextrins of less molecular complexity, with the simultaneous production of a corresponding amount of maltose.

After proving that the dextrins can be submitted to frequent dissolution in water, evaporation and precipitation with alcohol without being hydrolysed, the authors proceed to examine the action of malt extract upon the separated dextrins, the experiments being all carried out quantitatively. They find, when a starch transformation is separated into two or any desired number of fractional parts by means of precipitation with alcohol, that the mean maximum degrading action of malt extract upon the fractions separately is the same in amount as the possible degradation, *cæteris paribus*, of the original solution of the starch products. The degradation is measured by the amount of maltose produced, every experiment being carried out optically as well as chemically.

The authors conclude that O'Sullivan's statement that the dextrins behave differently with malt extract when isolated and when in solution with the other products formed simultaneously with them is incorrect, and that the dextrins which O'Sullivan isolated cannot be, as he supposed, the dextrins corresponding to his particular equations. This is shown by the fact that they did not yield the right amount of maltose on treatment with malt extract at the lower temperatures, and that in all transformations giving a materially higher angle for the products than 162·6°, it can be proved by fractionation with alcohol that the dextrins are not homogeneous, some belonging to a higher position and some to a lower in the polymeric series. In fact, all such transformations are of a mixed character, owing to the starch products not being simultaneously affected. Notwithstanding the fact that the reaction appears to have a tendency to be arrested at certain points corresponding to particular equations, if the malt-extract is treated in various ways prior to saccharification, yet above No. 8, which is a perfectly definite one, no sharp line of demarcation can be drawn between the equations, the possible number of which must be greater the larger the size of the starch molecule.

By submitting a separated dextrin, or a mixture of dextrins, to the

action of malt extract at 50—60°, and determining the amount of degradation experienced, it is possible to determine the actual or mean position in the polymeric series—the *actual* position if the dextrin be homogeneous, the *mean* position if it be a mixture. In this way an examination of the dextrin of a beer which has undergone the primary fermentation will indicate very approximately the angle, and hence the original percentage composition of the starch products of the mashing process.

The authors have attempted to prepare dextrin free from reducing power by Bondonneau's cupric chloride method. They have, however, never succeeded in entirely destroying the reducing power by this method, which they condemn from the fact that it is almost impossible to avoid hydrolysing the dextrin when employing it. They have succeeded in preparing dextrins free from reducing power by treatment with alkaline mercuric cyanide, and if this process is properly performed the dextrin is obtained in the same molecular state as before purification, *i.e.*, it is not hydrolysed, but yields with malt extract at 50—60° as much maltose as before treatment. The specific rotatory power of the purified dextrin approximates very closely to $[\alpha]_{j3\cdot86}216°$.

The dextrins are not directly fermentable by yeast, but require first to be hydrolysed. Some species of Saccharomyces, *e.g.*, *S. ellipticus* and *S. Pastorianus*, have the power under certain conditions of hydrolysing the higher dextrins, and fermenting the maltose so produced. The *Saccharomyces cerevisiæ* of the "high fermentation" possesses this power only to a very limited extent.

When the action of malt extract upon starch paste is limited, a *third body* is always found amongst the products of transformation, besides maltose and dextrin; it is more soluble in alcohol than the dextrins, and has a specific rotatory power of $[\alpha]_{j3\cdot86}193\cdot1°$, and a reducing power of $\kappa_{3\cdot86}21\cdot1$, corresponding to an apparent composition of 34·6 per cent. maltose and 65·4 per cent. dextrin. It is completely hydrated to maltose by the action of malt extract at 50—60°. The authors have no doubt that this substance is identical with one prepared by Herzfeld in an impure state, and described by him as *maltodextrin*.

Although the optical and reducing properties of maltodextrin seem to indicate that it is a mixture of maltose and dextrin, the following facts conclusively forbid such an assumption:—

1. A mixture of maltose and dextrin having the same optical character and reducing power as maltodextrin is separable into its constituents by a single judicious treatment with alcohol; whereas maltodextrin is not separable into maltose and dextrin by any possible treatment with alcohol, but is dissolved and precipitated as a homogeneous substance.

2. From a mixture of maltose and dextrin it is possible by means of the *Saccharomyces cerevisiæ* of the high fermentation to ferment the maltose, leaving the dextrin untouched. Maltodextrin treated in a similar manner is unfermentable.

3. When a mixture of maltose and dextrin is submitted to the action of malt extract at 50—60° a residue of No. 8 dextrin is always left, the amount being greater the lower in the series the dextrin is. Maltodextrin, on the other hand, is, under similar conditions, entirely converted into maltose, its amylin constituent leaving no residual dextrin.

4. Maltodextrin is slowly diffusible, and passes unaltered through the septum, whereas a mixture of maltose and dextrin is separable by dialysis.

Although maltodextrin is unfermentable by the ordinary yeast of the high fermentation, the addition of a trace of malt extract enables that form of yeast readily to ferment it by previous hydration to maltose. Maltodextrin also undergoes slow fermentation when submitted to the action of certain forms of Saccharomyces, *e.g.*, *S. ellipticus* and *S. Pastorianus*.

The composition of maltodextrin may be expressed by the formula $\begin{cases} C_{12}H_{22}O_{11} \\ (C_{12}H_{20}O_{10})_2 \end{cases}$, that is, a maltose group united with two amylin or dextrin groups, each constituent group retaining its optical and reducing properties.

The authors believe that the molecule of starch cannot contain less than five times the group $(C_{12}H_{20}O_{10})_3$, and that the action of malt extract consists in a successive hydration and removal of the $(C_{12}H_{20}O_{10})_3$ group, leaving as residue a dextrin of decreasing complexity, until the last of the five ternary groups is reached, which is the dextrin of the stable No. 8 equation, and undergoes no further change except a comparatively slow hydration. The removal of the $(C_{12}H_{20}O_{10})_3$ groups is accomplished prior to their complete hydration, the ternary group being split off the dextrin residue when only one of its amylin subgroups is hydrated, forming free maltodextrin, thus :—

$$\underset{\substack{\text{One of the five}\\ \text{ternary groups}\\ \text{constituting starch.}}}{(C_{12}H_{20}O_{10})_3} + H_2O = \underset{\text{Maltodextrin.}}{\begin{cases} C_{12}H_{22}O_{11} \\ (C_{12}H_{20}O_{10})_2 \end{cases}}.$$

The maltodextrin is subsequently converted into crystallisable and fermentable maltose on further action of malt extract, providing this has not previously been heated above 65°, by the fixation of the elements of two more molecules of water—

$$\left\{\begin{matrix}C_{12}H_{22}O_{11}\\(C_{12}H_{20}O_{10})_2\end{matrix}\right. + 2H_2O = 3C_{12}H_{22}O_{11}.$$

Maltodextrin. Maltose.

The authors are engaged in a full examination of the properties of maltodextrin, an account of which they hope shortly to lay before the Society.

51. "Decomposition of Carbonic Acid Gas by the Electric Spark." By H. B. Dixon, M.A., and H. F. Lowe, B.A.

Various chemists have investigated the decomposition of carbonic acid by the electric spark. Experiments having shown that no explosion is propagated by a spark in a mixture of carbonic oxide and oxygen dried by standing over anhydrous phosphoric acid, it seemed of interest to repeat the experiments on the decomposition of carbonic acid when dried in a similar manner. Carbonic acid dried over anhydrous phosphoric acid was submitted to a series of induction sparks in a eudiometer by means of a chain composed of short pieces of platinum fused into small glass bulbs. The amount of decomposition varied from time to time, approaching no fixed limit. Similar results were found on introducing a Leyden jar into the secondary circuit of the Ruhmkorff, but the amount of decomposition was less.

On passing a series of induction sparks through a dried mixture of carbonic oxide and oxygen partial combination gradually took place, but no fixed limit was reached.

Two similar eudiometers were prepared and fitted with wires made of an alloy of platinum and iridium, each wire ending in a bulb about 2 mm. in diameter. The bulbs were brought to the same distance apart in the two tubes. On bringing an equal volume of dried carbonic acid into the two tubes, and sending a series of sparks from one Ruhmkorff coil through both tubes at the same time, the gases in the two vessels were found to be equally affected, their volumes varying exactly together so long as the pressure was kept the same in the two tubes. The more feeble the spark the greater was the decomposition of the carbonic acid found to be.

When 100 volumes of dried carbonic acid were brought into one tube, and 150 volumes of a dried mixture of carbonic oxide and oxygen were brought into the other, and a series of sparks were passed through both from the same coil, the volume of carbonic acid increased, and the volume of carbonic oxide and oxygen diminished until after some hours they became equal. On a further prolonged passage of the spark the two volumes altered together, sometimes increasing and sometimes diminishing, as the nature of the spark varied.

A coil of fine platinum wire was heated by an electric current to whiteness in dried carbonic acid. No permanent alteration of volume was produced. When a similar coil of platinum wire was heated in a mixture of dried carbonic oxide and oxygen, it glowed intensely for some minutes, and complete combustion was found to have taken place betwen the two gases. No flame was visible round the wires.

Discussion.

Mr. Cowper said that he could confirm Mr. Dixon's statements: on passing sparks through a dry mixture of CO and oxygen he had always noticed a blue glow around the wires, due to local action, but no explosion took place unless the gases had not been thoroughly dried.

Captain Abney inquired to what extent Mr. Dixon had heated the tubes before introducing both gases; it was well known that moisture condensed on the glass, which it was not easy to remove.

Dr. Armstrong said that Mr. Dixon's observations appeared, like those of Langer and Mayer on the action of chlorine on platinum, to support the view he had put forward in a previous discussion, that probably it was necessary to distingnish between two forms of chemical action, the one occnrring at high, the other at low temperatures. It was an important question whether the platinum played any part in the case under discussion; even without it, however, three things would still be present, since there would be CO, O_2 and O, whenever the spark passed.

Professor McLeod asked whether Mr. Dixon had observed the deposition of a dark brownish substance near the electrodes when sparks were passed through dry CO_2. He called attention to the fact that chromic chloride was rendered soluble in water by a trace of chromous chloride as an illustration of the influence exerted by a third body.

Mr. Donkin reminded the meeting of Sir B. Brodie's observations on the production of lower solid oxides of carbon when carbonic oxide was submitted to the action of the silent discharge in a Siemens tube.

Mr. Dixon said that he had heated his tubes above 100°, and had then introduced hot mercury; oxygen was next introduced and also the drying agent, and the wire was then heated to redness for some time. In his experiments he had not observed the formation of the deposit referred to. He had found that carbon monoxide was decomposed to the extent of only 0·5 per cent. by sparking.

52. "On the Influence of Silicon upon the Properties of Cast Iron." By Thomas Turner, Assoc. R.S.M.

The author has prepared "pure cast iron," that is, cast iron as free as possible from the ordinary impurities, by heating wrought iron with charcoal for about five hours. The composition of the product was C = 1·98, Si = 0·19, Mn = 0·14, P = 0·32, S = 0·35. The cast iron was then melted with suitable quantities of silicon pig-iron containing C = 1·81, Si = 9·80, Mn = 1·95, P = 0·21, S = 0·04, and from the product test-bars of about 1·1″ diameter and 19·7″ long were prepared.

These bars, tested by Professor Kennedy with the University College testing machine, gave the following results:—

Silicon, per cent.	Breaking Load. Tons per square inch.	Modulus of Elasticity.
0	10·14	25·79 millions.
0·5	12·31	28·67 „
1	12·72	31·18 „
2	15·70	23·56 „
2·5	14·62	25·45 „
3	12·23	21·15 „
4	11·28	15·64 „
5	10·16	18·72 „
7·5	5·34	14·75 „
10	4·75	13·93 „

These results show that, contrary to the generally accepted views on this subject, a suitable addition of silicon to cast iron improves the tensile strength of the metal. Any further addition, however, beyond 2·5 per cent., causes a gradually increasing deterioration.

Each test-piece was analysed after fracture, and the results of these analyses are given. They show that the actual silicon and carbon content is always very near to that desired, while the sulphur and phosphorus are fairly constant. The manganese increases gradually up to 1·95 per cent.

It is shown that the graphitic carbon is increased by the addition of silicon, and consequently the iron passes in character from white to grey. The addition of silicon renders the metal more fluid, and gives smoother, finer castings; and, in moderate quantity, undoubtedly renders the metal more sound. In larger quantities, however, it renders the metal brittle.

Discussion.

Mr. Spiller said a Blue-book was published about 1860, by Sir

Frederick Abel, containing an account of similar experiments with cast-iron. He had taken part in those experiments. The results arrived at were very different from those now put forward: in fact, he was inclined to question altogether Mr. Turner's conclusions, as he was not satisfied with the method of testing adopted, particularly the shape and size of the testing bars.

Dr. Wright emphasised the fact that the figures adduced showed the carbon to be in a very different condition though the same in amount in the different specimens tested; he did not think that the specimens were comparable.

Mr. Turner, in reply, said that unfortunately he was not acquainted with the Blue-book referred to, and that it was not mentioned in the metallurgical books. [Mr. Spiller, interposing, said the results were quoted in *Watt's Dictionary*.] He had acted under the advice of engineers in preparing the test bars. It was true the carbon was in a different condition, but the difference was due to the silicon.

53. "Eleven Months' Experience with Toughened Glass Beakers." By R. J. Friswell.

In July, 1884, twenty-one beakers were purchased of the Toughened Glass Company, working De la Bastie's patents. One of these was broken by an accident and twenty were taken into use in the laboratory of the Atlas Works. They had the form of thin tumblers furnished with a lip. The bottom is about three times as thick as the sides, and weight for weight they are $2\frac{1}{2}$ times as heavy as the Bohemian beaker of about the same capacity.

It was stated on behalf of the makers that they would stand boiling over the flame of a rose burner while supported on wire gauze, but as one of them burst soon after he began to use them, on pouring hot water into it, the more severe treatment was never tried, and they were relegated to ordinary use.

Of late they have been considerably in use in collecting some somewhat tarry distillates, and since then have begun to show evidences of rapid decay. Some slight signs of this had been noticed early in the career of some of them, but as it principally took the form of slight surface corrosion and dulling of the glass, it was attributed to the well-known action of caustic alkaline solutions.

The new action was different, the sides exhibiting a mass of exceedingly minute fissures, so close together and running so completely over the surface of the beaker that it had the appearance of being covered with a tissue of spider's web. The next change consisted in the surface of the glass completely exfoliating, so that on rubbing the finger along the surface, a mass of minute plates could

be detached. At length one of the beakers was attacked in this way over about one-third of its surface, and the boundary between the attacked part and that simply fissured was a sharp line passing up both sides and across the bottom. He at first thought that this indicated imperfect annealing or tempering, and, in fact, showed the depth of immersion in the oil-bath.

On a little consideration this appeared highly improbable, and he accordingly, though with little hope of solving the mystery, resolved to try whether the two liquids used to clean the glasses when very dirty had anything to do with it.

A beaker was half filled with caustic soda solution, another with strong sulphuric acid 1·845, and another with 25 per cent. sulphuric acid.

At the end of 72 hours neither the caustic soda nor the weak sulphuric acid had produced any effect, but the beaker with the strong H_2SO_4 was entirely ruined by an extensive exfoliation which left plates sticking up from the surface from $\frac{1}{4}$ mm. to $\frac{1}{2}$ mm. in height.

The beaker in which the 25 per cent. acid had been was washed and placed on its side to dry on a piece of thick grey filtering paper lying on top of a copper water-oven. In about one hour's time a broad strip up the side in contact with the paper had exfoliated both inside and outside. It was moistened with water, turned over and replaced. In about half an hour another strip of exfoliation had begun.

Near the edge of the vessel the scales took the form of hairs 1—2 mm. long, and completely curved over at the upper end in the form of the letter C.

About ten days back one of the slightly fissured beakers burst spontaneously, and a few days after another followed suite, both containing water at the time.

The thick bottom of one of these was a reticulated mass of cracks; when obliquely illuminated each crack shows as a slight depression of the surface.

The result of eleven months' use may thus be summarised:

Of 20 beakers—

2 burnt spontaneously	= 10	per cent.
1 ,, on hot water being poured in ..	5	,,
6 useless from fissures and enfoliation ..	30	,,
8 are in good condition	40	,,
3 have been broken by unknown means.	15	,,
20	100	

Taking into consideration the loss of confidence caused by the

high percentage of spontaneous bursting, it may be said that toughened glass is a complete failure in the laboratory.

The following Papers were taken as read:—

54. "Bromo-derivatives of Diphenyl, Tolylphenyl and Ditolyl." By Prof. Carnelley and Andrew Thomson.

Tribromodiphenyl, $C_6H_4Br{\cdot}C_6H_3Br_2$ (1 : 4—1 ? ?), prepared by the action of excess of bromine on diphenyl dissolved in 1 : 4 tolylphenyl, crystallises in colourless silky needles (m. p. 90°), and is very difficultly soluble even in hot alcohol. On oxidation it yields 1 : 4 bromobenzoic acid (m. p. 248°).

The authors have obtained two modifications of *diparadibromodiphenyl* by the action of bromine on pure diphenyl. They both melt at 162°, and are in all respects identical, except that the one crystallises in prisms and the other in octohedra. The latter does not appear to have been previously observed.

Monobromo-(1—4)*tolylphenyl*, $C_{13}H_{11}Br$, obtained by brominating he pure hydrocarbon, crystallises in small pearly plates (m. p. 131°), and is almost insoluble in cold, and only difficultly soluble in hot alcohol, but very easily soluble in benzene.

Two isomeric modifications of *dibromo*-(1 — 4)*tolylphenyl*, $C_{12}H_7Br_2{\cdot}CH_3$, were obtained by the action of bromine on the 1—4 hydrocarbon, but it was not found possible to separate them. On oxidation of the mixture two isomeric modifications of dibromophenylbenzoic acid, $C_{12}H_7Br_2{\cdot}COOH$, were obtained. The one melted at 202° and the other at 232°.

Monobromo-(2—4′)*ditolyl*, $C_6H_4Me{\cdot}C_6H_3BrMe$ (Br ?), was prepared by the action of bromine on the hydrocarbon. It crystallises in fine interlacing microscopic needles (m. p. 94°). It is only very slightly soluble in cold alcohol, and difficultly soluble in hot, but easily soluble in ether or benzene. On oxidation it yields monobromoterephthalic acid (m. p. 306°).

Monobromo-(2—4′)*ditolyl*, $C_6H_4Me{\cdot}C_6H_3BrMe$ (Br = 4), an oil which, on oxidation, gives *monobromodiphenic acid*,

$$C_6H_4(COOH){\cdot}C_6H_3Br{\cdot}COOH,$$

melting at 215°, and this, on further oxidation, is converted into 4 : 2 : 1 *monobromophthalic acid*, $C_6H_3Br(COOH)_2$ melting at 203°.

Dibromo-(2—4)′*ditolyl*, $C_{14}H_{12}Br_2$, was obtained by the action of the calculated quantity of bromine on the hydrocarbon. It crystallises in beautiful long, almost hair-fine, lustrous needles (m. p. 156°). This dibromo-compound behaves in a remarkable manner on oxidation, giving first a brilliant yellow compound (m. p. 170°) having the

composition of a diketone, $C_{12}H_6Br_2(CO)_2$, isomeric with dibromophenanthraquinone, but having a different orientation. On further oxidation the dibromoditolyl gives a brilliant yellow product, very similar to the diketone just described, but melting at 201°, and having the composition of a dibromodiphenic acid, $C_{12}H_6Br_2(COOH)_2$, but not really having the latter constitution, as it does not seem to possess the properties of an acid.

55. "Note on the Influence of Strain upon Chemical Action." By Prof. Carnelley and James Schlerschmann.

The experiments were undertaken with the object of determining whether strain had any influence upon chemical action. It appeared, *à priori*, not impossible that there might be an effect such as would increase chemical action, for presumably any condition which would tend to lessen the attractive force between the particles of an iron wire, for example, would also assist the action of acids, &c., on such a wire. Two series of experiments were made as follows:—

Series A.—In each experiment copper wire (18 gauge) was exposed for three hours to the action of 100 c.c. of a 10 per cent. solution of ammonium chloride. In one set of experiments the wire was kept stretched by a weight of 2 lbs., and in a second set by a weight of 28 lbs. The copper dissolved by the liquid was determined colorimetrically with potassium ferrocyanide.

The results were as under:—

		Strain on Wire = 2 lbs.	Strain on Wire = 28 lbs.
Experiment (1) ..	Copper dissolved	= 5·5 mgrms.	5·5 mgrms.
„ (2) ..	„ „	= 5·1 „	5·1 „
„ (3) ..	„ „	= 5·2 „	5·2 „

Series B.—In each experiment iron wire (19 gauge) was exposed for three hours to the action of dilute sulphuric acid (1 : 25). In one set of experiments the wire was kept stretched by a weight of 2 lbs., and in a second set by 56 lbs. The iron dissolved was determined colorimetrically by potassium ferrocyanide. Results as under:—

		Strain on Wire = 2 lbs.	Strain on Wire = 56 lbs.
Experiment (4) ..	Iron dissolved	= 2·0 mgrms.	1·8 mgrms.
„ (5) ..	„ „	= 2·0 „	2·0 „
„ (6) ..	„ „	= 2·0 „	2·0 „

These experiments show, therefore, that strain exerts no perceptible influence upon chemical action, or, at least, not under the conditions above described.

56. "On the Non-existence of Gaseous Nitrous Anhydride." By William Ramsay, Ph.D.

In replying to Dr. Lunge's criticisms on a recent paper by Mr. Cundall and himself, the author points out that Dr. Lunge's proofs of the existence of gaseous nitrous anhydride all involve the presence of sulphuric acid; and moreover that the behaviour of Dr. Lunge's nitrous anhydride, acknowledged by him to be a body at least capable of partial dissociation, is unique, inasmuch as the extent of its dissociation is not increased by rise of temperature. The author then describes experiments which prove that on mixing gaseous nitric peroxide with nitric oxide, no diminution of volume is observable; as reaction between these gases would imply contraction, it is concluded that no reaction takes place, so long as they are gaseous. But on cooling the mixture of gases a deep blue liquid is condensed, which is doubtless a mixture of liquid nitrous anhydride with liquid nitric peroxide; it is thus seen that on assuming the liquid state, reaction is possible.

57. "On the Causes of the Decrepitations in Samples of so-called Explosive Pyrites." By B. Blount.

Having obtained certain samples of pyrites showing in a marked manner the phenomenon of decrepitation when heated to moderate temperatures, the author of the paper examined these samples to determine, if possible, whether the decrepitations were produced (1) By the expansive force of water contained in the cavities of the ore, or (2) the expansive force of gas similarly contained. Weighed quantities of the pyrites were heated in a Liebig's tube to 100° C., and the gas or vapour evolved collected in weighed absorption-tubes. From these experiments it was found that moisture and carbon dioxide were given off in the decrepitation of the pyrites. The amounts of water and CO_2 given off were not in the proportions corresponding to the formula H_2CO_3, the CO_2 being much in excess of the moisture. The cavities are apparently very widely and not at all regularly, distributed throughout the samples. The author concludes that (1), that the decrepitations are due to the presence of CO_2, together with greater or less quantities of moisture; (2), that the CO_2 is confined at high pressures, probably sufficient to liquefy it; (3), that the usual temperature at which the pyrites begins to decrepitate is 30—35° C.

58. "On the Specific Action of a Mixture of Sulphuric and Nitric Acids upon Zinc in the Production of Hydroxyamine." By E. Divers, M.D., F.R.S., and T. Shimidzu, M.E.

No quantitative experiments appear to have been published upon

the variable activity of zinc towards sulphuric acid. Carefully cleaned sheet-zinc of one quality may show the greatest differences in the rate at which it dissolves in sulphuric acid of a certain dilution. In five minutes, four times as much zinc has been found to dissolve, from equal surfaces, in one experiment as in another. In this case, 15 per cent. sulphuric acid was used. With weaker acid the difference would sometimes prove much greater, as when in 20 minutes' immersion in 3 per cent. acid, the dissolved metal was 10 times greater in one case than in another, under conditions arranged alike. But these differences diminish as the duration of the dissolution is prolonged. In 20 minutes the greatest difference observed with 15 per cent. acid has been but little more than four to three.

Zinc that proved tolerably sensitive to sulphuric acid from the first, showed a solubility in the acid of different strengths that was approximately in proportion to the dilution of the acid; but zinc, nearly inactive in 3 per cent. acid, dissolved in 15 per cent. acid, in 15 minutes, 12 times as much as it did in $7\frac{1}{2}$ per cent. acid. These differences in activity towards sulphuric acid are shown also by granulated zinc, but not to the same extent. They do not seem to be due merely, or even to a great extent, to differences in composition of commercial zinc, but to be galvanic phenomena. Nitric acid is also irregular in its action upon zinc, but much less so than sulphuric acid.

The action of a mixture of nitric and sulphuric acids is very much more rapid than that of either of these acids, of similar dilution, by itself. Thus, dilute nitric acid mixed with three times its volume of a dilute sulphuric acid, of less average activity upon zinc than itself, formed a mixture at least five times as active as the dilute nitric acid by itself was. The experiments were so arranged that there should be no material rise in the temperature, as that would of itself have greatly increased this disproportion.

Both the nascent hydrogen hypothesis, and that of the sulphuric acid serving to keep unreduced nitric acid free, entirely fail to explain such a superior activity in the mixed acids; and the only view of the matter that appears sufficient for the purpose is, that the mixed acids exert a specific action upon the zinc, by virtue of which the sulphuric acid is decomposed by the combined action upon it of the nitric acid and the zinc. Alone, these bodies are inactive, or nearly so, upon it, but together they at once decompose it, just as hydrochloric acid and selenium together decompose sulphuric acid, or as nitric oxide and stannous chloride together decompose hydrochloric acid.

Hydroxyamine, in acid solution, is not decomposed by zinc, as it has hitherto been assumed to be. Its solution may even be boiled upon zinc for some time, provided it is kept acid, without undergoing

appreciable change. As a consequence of this fact, the hydroxyamine formed by zinc in a mixture of nitric and sulphuric acids, remains in the solution for some minutes unaffected, and only declines in quantity as the sulphuric acid approaches neutralisation. Even in absence of acid, hydroxyamine in solution is only slowly decomposed by contact with zinc, so long as the solution is cold. In hot solutions it is much more rapidly changed.

The production of ammonia from nitric acid by zinc in presence of sulphuric acid must be regarded as the result of the direct and independent action of the nitric acid upon the zinc. It seems also nearly certain that hydroxyamine is the sole product of the specific action of the mixed acids, and that it would not be producible by zinc alone from truly pure nitric acid.

Variations in the proportions of hydroxyamine obtained from nitric acid by treating it with sulphuric acid and zinc depend very largely upon undetermined peculiarities in the zinc. One zinc may prove three times as productive as another. This difference in productiveness does not appear to depend altogether upon differences in the activity of the zinc towards sulphuric acid, or upon differences in composition. Lead seems to be indifferent, while iron sometimes acts injuriously.

The production of hydroxyamine is favoured by heat, nearly boiling solutions giving somewhat better yields than cold ones, provided that the sulphuric acid is not too much diluted, and that it is in sufficient excess over the nitric acid; increase in its amount is without effect upon the yield of hydroxyamine. The degree of dilution of the nitric acid has no apparent effect upon the yield of hydroxyamine. An investigation of the effects of varying circumstances upon the yield of hydroxyamine from nitric acid by the action of zinc and sulphuric acid is greatly impeded by the irregular behaviour of what, in other respects, appears to be the same quality of the metal.

59. "On the Action of Pyrosulphuric Acid upon certain Metals." By E. Divers, M.D., F.R.S., and T. Shimidzu, M.E.

New reasons for considering liquid or solid sulphur trioxide as [S_2O_6] rather than as [SO_3], are afforded by the results of some experiments upon the reaction of pyrosulphuric acid with silver, mercury and copper.

When carefully freed from sulphuric acid and moisture, sulphur trioxide is without action upon these metals; it is otherwise when a little sulphuric acid is present. Silver dissolves freely in melted pyrosulphuric acid without evolution of gas. The products are silver sulphate and sulphur dioxide, which remains dissolved in the fuming

acid, in which it is very soluble. Mercury behaves like silver, but, as its sulphate is less soluble in sulphuric acid, this soon begins to separate. Also, when the solution of the mercury is poured into water, there is obtained not sulphur dioxide, but metallic mercury, besides mercurous sulphate. The cause of this difference is merely that the sulphur dioxide reduces some of the mercurous sulphate when the two substances come in contact with the water.

The reaction between silver or mercury and the fuming acid is clearly one between it and sulphur trioxide, since the metal is practically unacted upon by cold sulphuric acid itself. The metal displaces the radical sulphuryl, which then becomes sulphur dioxide :—

$$(SO_2)SO_4 + 2Ag = Ag_2SO_4 + SO_2.$$

Pure sulphur trioxide cannot act upon these metals because of the insolubility of the sulphate in it.

The propriety of viewing the reaction as one between the sulphur trioxide and the metal is further shown by the behaviour of copper with pyrosulphuric acid. Copper is acted upon only until it gets coated with a mixture of sulphate and sulphide. Copper sulphate is almost insoluble in sulphuric acid. The sulphide results from reaction between sulphur dioxide and copper. Divers has already in a recent paper advanced the view that the action of hot sulphuric acid upon copper, mercury, and silver is in reality one between the metal and sulphur trioxide, into which and water, sulphuric acid so readily dissociates at a moderate heat.

The treatment in the cold of mercury with pyrosulphuric acid is recommended for the preparation of mercurous sulphate.

60. "On the Constitution and Reactions of Liquid Nitric Peroxide." By E. Divers, M.D., F.R.S., and T. Schmidzu, M.E.

It is improbable that when hot gaseous nitric peroxide [NO_2] condenses to the liquid peroxide, [N_2O_4], the two nitrogen-atoms directly unite, because the direct combination of two atoms of nitrogen in the simple body itself, or in compounds, is a very stable one. But evidence is still wanting that the peroxide is nitrosyl nitrate, [$ON{\cdot}O{\cdot}NO_2$]. The only reaction that points to this constitution is that between the peroxide and sulphuric acid—$N_2O_4 + H_2SO_4 = HNO_3 + (ON)HSO_4$, in which it changes into nitrosyl sulphate and hydrogen nitrate. This want of evidence is greatly lessened by the knowledge of the reactions between nitric peroxide and some metals.

Mercury treated with dry rectified nitric peroxide is converted into mercurous nitrate, with more or less mercuric nitrate, nitric oxide being liberated. Silver is superficially converted into nitrate also

with the evolution of nitrous oxide; and neither in the case of mercury nor of silver is nitrite formed. The reaction is, therefore, the displacement by metal of nitrosyl in its nitrate.

The reaction with copper appears to be the same, but its exact determination is rendered difficult by the instability, in contact with water, of cuprous nitrate, for that is the copper salt which appears to be formed. The product treated with water gives metallic copper and cupric nitrate, and with concentrated alkali, alkali nitrate and cuprous hydroxide. But other changes occur, the cuprous hydroxide seeming to reduce some nitrate to ammonia, and cupric nitrate solution reacts with finely divided copper to form nitric oxide and basic copper nitrate.

The action of heat upon silver nitrite has been reinvestigated. The salt has been heated in absence of air. The results confirm those formerly got by Divers. Heated only to 125°, it slowly decomposes to silver nitrate, silver and nitric oxide. Heated strongly, it changes, to a large extent, into nitric peroxide and silver, although some silver nitrate and nitric oxide are formed. The fact, formerly ascertained by Divers, that silver nitrite, heated cautiously in a confined space, can, by absorption of oxygen from the air, become nitrate without the formation of much free silver, is considered to indicate that the formation of nitrate is due to the action of nitric peroxide upon silver, and not to the oxidation of nitrite. It is regarded as unlikely that silver nitrite unites directly with free oxygen, and it is shown that nitric peroxide has no action on silver nitrite. If silver were not converted into the nitrate, it is inexplicable why, after 78 hours' exposure to a temperature decomposing silver nitrite, it should be possible to have only a small fraction of the silver in the metallic state.

61. "On the Behaviour of Stannous Chloride towards Nitric Oxide, and towards Nitric Acid." By E. Divers, M.D., F.R.S., and T. Haga.

In contradiction to statements and assumptions hitherto made, it is asserted that tin and hydrochloric acid do not convert any part of either nitric oxide or nitric acid into ammonia. Also, that stannous chloride does not form ammonia from these bodies—at least, not below or up to 100°. Thirdly, that hydroxyamine is not converted to ammonia, or otherwise affected, by either hydrochloric acid and tin, or hydrochloric acid and stannous chloride, whether in hot or in cold solution.

Ammonia is formed, however, when nitric oxide is treated with either tin or stannous chloride and acid, in presence of oxygen. To

want of care in excluding air, and to indifference as to the purity of the nitric oxide employed, must be attributed the experience of previous workers that ammonia is formed from nitric oxide. For von Dumreicher's statements that hydroxyamine is rapidly converted into ammonia by acid stannous chloride at 100°, and that nitric acid yields ammonia when treated with that reagent, no explanation has suggested itself, by which they can be made consistent with the experiences here recorded.

Besides hydroxyamine, some nitrogen is produced by the action of stannous chloride upon nitric oxide. Strange to say, at 100°, stannous chloride is without any action upon nitric oxide, except the doubtful production of a trace of ammonia. At common temperatures, there is probably an unstable compound produced, such as—$[Cl_2Sn(ON : SnCl_2)_2]$, and this, decomposing with hydrochloric acid, yields stannic chloride and hydroxyammonium chloride. Stannous chloride is readily, though slowly, converted to stannic chloride by nitric oxide.

Nitric acid is only acted upon by stannous chloride in presence of strong hydrochloric acid solution, not in presence of dilute acid. Nitrosyl chloride would thus appear to be the source of the hydroxyamine, and not the nitric acid. The action of the nitrosyl chloride upon stannous chloride will be that of its two radicles. This action will be further examined, but it already seems to favour the view held by Divers, that the nitrogen of nitric acid is tervalent rather than quinquivalent.

62. "Preliminary Note on the Reaction between Mercurous Nitrate and Nitric Oxide, and between Mercurous Nitrate and Nitrites." By Edward Divers, M.D., F.R.S., and Tamemasa Haga.

It has been known for, perhaps, half a century, that mercurous nitrate yields metallic mercury when treated with a solution of alkali nitrite, and this reaction has been always regarded as one of oxidation of the nitrite by reduction of the mercury salt. Obviously true as this seems to be, we believe we can, even in this preliminary note, show that, nevertheless, it is not true.

When, with exclusion of air, pure nitric oxide is passed into a solution of mercurous nitrate in dilute nitric acid, *a precipitation of metallic mercury slowly takes place, and hydroxyamine is formed in quantity, but no ammonia.* The solution contains mercuric nitrate. By prolonging the contact of gas for many hours, beautiful long yellow prisms crystallise out, while the metallic mercury still remains. The mother-liquor now contains a mercury salt of specific reactions, together with ammonia, but no longer any hydroxyamine. With

hydrogen sulphide, it yields sulphur and a brown precipitate, which, when heated, effervesces and blackens. With potassium hydroxide, a precipitate, first reddish, then greyish, is obtained. The yellow crystals effervesce with acids, and are slowly changed by them. In this change, a little black matter is formed, and with hydrochloric acid, both mercuric and mercurous chlorides are obtained. The black matter, heated again with fresh hydrochloric acid, yields metallic mercury. The gas evolved is pure nitric oxide. Neither ammonia nor hydroxyamine can be got from the crystals. Boiled with water, they effervesce, and partly dissolve, and metallic mercury separates. Even cold water slowly separates mercury from them. Heated dry, they decompose much as do mercury nitrates. We hope to offer the Society a fuller account of this yellow salt in the early part of next year. We wish now only to comment specially upon the first stage of the reaction.

In the first stage of the reaction, we have the remarkable phenomenon, not of nitric oxide acting as a reducing agent, for, on the contrary, much of it gets hydrogenised, but of *nitric oxide precipitating mercury from its salt*—$(HgNO_3)_2 + 2NO = 2(NO)NO_3 + 2Hg$. We see no means of rejecting that equation, remarkable as it undoubtedly is. The nitrosyl nitrate, here assumed to form, will at once decompose with water and mercurous nitrate into hydroxyammonium nitrate and mercuric nitrate, perhaps in the way represented by the following equation :—

$$4(HgNO_3)_2 + 8HNO_3 + 2(NO)NO_3 = 8Hg(NO_3)_2 + 2(HONH_3)NO_2.$$

The after-reaction is probably one between mercuric nitrate and nitric oxide. The destruction of hydroxyamine presents no difficulty.

In the case of the long-known precipitation of mercury by a nitrite, we find that, provided the nitrite be added gradually to a concentrated solution of mercurous nitrate, kept in considerable excess, *it is accompanied by an abundant production of hydroxyamine*. The reaction can no longer, therefore, be treated as one of reduction of mercury salt by the oxidation of a nitrite. We are not yet prepared to speak with any certainty as to the exact nature of this reaction. The free acid of the mercury solution will probably yield alkali nitrate and nitric oxide—$3KNO_2 + 2HNO_3 = 3KNO_3 + H_2O + 2NO$, and then the nitric oxide will react with the mercurous salt, as we have found it to do.

A hydrochloric acid solution of cuprous chloride is unaffected by nitric oxide.

63. "On some Derivatives of Anthraquinones." By A. G. Perkin and Dr. W. H. Perkin, jun.

The authors have studied the products of the destructive distillation of sodium anthraquinone sulphonate. By treating the crude distillate with boiling baryta-water they have separated metoxyanthraquinone. The residue contains anthraquinone, which can be extracted by glacial acetic acid, leaving a body of the formula $C_{28}H_{14}O_6$, which also dissolves, though very sparingly, in acetic acid, crystallising in minute yellowish-red needles. This compound yields anthracene when distilled with zinc-dust; it dissolves in cold sulphuric acid, forming an intense magenta-red coloured liquid; on oxidation with chromic acid it is converted into the compound $C_{14}H_6O_4$. This latter forms colourless plates melting at 292°; it is insoluble in alkalis; it yields anthracene when distilled with zinc-dust, and it reacts with phenylhydrazine. The authors are inclined to regard it as an orthoquinone of anthraquinone.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Official Year-Book of the Scientific and Learned Societies of Great Britain and Ireland; London, 1885: from the Publishers, Messrs. C. Griffin and Co.

The Copper-Bearing Rocks of Lake Superior. By R. D. Irving; Washington, 1883: from the U.S. Geological Survey.

143 Pamphlets by various Swedish and Danish Investigators, comprising 12 on Physical Chemistry, 37 on Mineralogical Chemistry, 48 on Inorganic Chemistry, and 46 on Organic Chemistry: from Prof. Clève.

II. *By Purchase.*

A Text-Book of Pharmacology, Therapeutics, and Materia Medica. By T. Lauder Brunton. London, 1885.

A Treatise on the Principles of Chemistry. By M. M. Pattison Muir. Cambridge, 1884.

Experimental Researches in Electricity. Vol. II. By M. Faraday. London, 1884.

Titles of papers of interest to chemists recently read before Societies in the United Kingdom:—

"The Action of Tidal Streams during Diffusion of Salt and Fresh Water." Part II. By T. Andrews.

"The Removal of Micro-organisms from Water." By Dr. P. Frankland.

"On the Influence of Temperature on the Heat of Dissolution of Salts in Water." By Prof. Tilden, F.R.S.

"On Radiant Matter Spectroscopy." Part II—Samarium. By W. Crookes, F.R.S.

"The Vortex Ring Theory of Gases." By Prof. J. J. Thomson, F.R.S.

Royal Society of London, June 18th.

NOTICE TO FELLOWS.

Library.—The Library will be closed in the evening during July and September, and entirely during August for the re-arrangement of the books. Fellows are requested to return all books not later than July 31st.

HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY, ST. MARTIN'S LANE.

ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 12. Session 1885-86.

November 5th, 1885. Dr. Hugo Müller, F.R.S., President, in the Chair.

Mr. Leonard de Koningh was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Richard Haliburton Adie, Trinity College, Cambridge; James Sabin Adriance, M.A., Williams College, Williamstown, Mass.; Charles Morton Aikman, 12, South Parade, South Kensington; James Anderson, Moone Ponels, Victoria; Edward B. Clark, Rangoon; M. J. R. Dunstan, 24, Sinclair Road, W.; George E. R. Ellis, Haversham Grammar School, Milnthorpe; James Epps, junr., The Homestead, Ross Road, South Norwood; Lazarus Fletcher, 19, Avenue Gardens, Mill Hill Park, Acton, W.; William L. Gadd, 50, Richmond Grove, Manchester; Gilbert Print Girdwood, 28, Beaver Hall Terrace, Montreal, Canada; W. H. Greene, M.D., 3225, Sansom Street, Philadelphia, U.S.A.; Ernest William Harvey, Thomlie Villa, Wishaw, N.B.; George Hirst, 140, Rock Street, Sheffield; Thomas Holgate, Eldon Villa, Batley; Edward E. Howard, Denia Lodge, West Croydon; Mathew Hunter, B.A., Cowside, Settle; George H. Hurst, 11, Cable Street, Salford; John Cecil Husband, Berwick-on-Tweed; Lewis Gordon Paul, Ph.D., Holyrood, Upper Norwood; Leonard Peckitt, 53, South 6th Street, Reading, U.S.A.; Charles Ranken, Stockton Road, Sunderland; Luther R. Scammell, 42, King William Street, Adelaide; James Sim, 77, Dee Street, Aberdeen; Henry J. Staples, Spondon, Derby; Stephen Stephenson, Llyn-y-mawn, Holywell, Flint; Henry Stocker, Peases West Crook, Durham; Thomas B. Tyson, 50, King Street, Penrith; Henry Collins Williams, 56, Green Lanes, Stoke Newington; Charles F. Young, 43, Manchester Old Road, Middleton.

The following papers were read : —

64. "The Influence of Silicon on the Properties of Cast Iron." Part II. By Thomas Turner, Assoc. R.S.M.

The paper is a continuation of one recently published (*Chem. Soc. Trans.*, 1885, 577).

An account is given of experiments on the relative density, hardness, working qualities and crushing strength of the metal, and the reason of the variations noticed is discussed.

The relative density was determined both in mass and in small fragments. In the first case, cylinders 3″ × 1″ were employed, and the turnings from the cylinders were used for a second determination. In iron possessing great tenacity the density was slightly increased, but with less tenacity the density was decreased by the force exerted in turning the metal. The hardness was measured by the weight in grams necessary to produce a scratch with a cutting diamond. The influence of silicon is shown to be quite regular, the greatest softness being produced by from 2 to 3 per cent. The working qualities are taken from the observation of a skilled workman, and agree very closely with the hardness as before determined.

The crushing strength tests were performed by Prof. Kennedy on cylinders 3″ × 0·75″, and sketches are given of the fractured specimens. The influence is tolerably regular, and of the kind previously observed: the maximum value being reached with 1 per cent. of silicon.

In the following table a summary is given of the chief results :—

Silicon per cent.	Relative density* of cylinders, 3″ × 1″.	Relative density* of turnings from cylinders.	Relative hardness.	Crushing strength. Breaking load per sq. in.	
				Pounds.	Tons.
0	7·560	7·719	72	168,700	75·30
0·5	7·510	7·670	52	204,800	91·42
1	7 641	7·630	42	207,300	92·54
2	7·518	7·350	22	135,600 139,000	60·53 62·05
2·5	7·422	7·388	22	172,900	77·18
3	7·258	7·279	22	128,700	57·45
4	7·183	7·218	27	106,900	47·74
5	7·167	7·170	32	103,400	46·16
7·5	7·128	7·138	42	111,000	49·55
10	6·978	6·924	57	76,380	34·10

* Water at 20° C. = 1.

The author draws the following conclusions from these results.

1. That a suitable small addition of silicon to cast iron almost entirely free from silicon is capable of producing a considerable improvement in the mechanical properties of the metal.

2. That in these experiments the maximum values are probably reached with the following amount of silicon:—

Crushing strength	about	0·80 per cent.
Modulus of elasticity	„	1·00 „
Relative density (in mass) ..	„	1·00 „
Tensile strength	„	1·80 „
Softness and working qualities	„	2·50 „

3. That when general strength is required the amount of silicon should not vary much from about 1·4 per cent.; but that when special softness and fluidity are desirable, about 2·5 per cent. may be added. Even in the latter case, however, any increase upon 3 per cent. must be dangerous.

These conclusions are only strictly true under the circumstances of the author's experiments, but he hopes shortly to bring forward evidence from independent investigations to support his results.

The cause of these results is discussed. The author is decidedly of the opinion that the production of graphitic carbon is not the only cause of these differences, but that, in addition to the indirect effect owing to the production of grey iron, the suitable addition of silicon has a direct and beneficial influence upon the mechanical properties of the metal.

Discussion.

Dr. Wright inquired whether any experiments had been instituted to determine the influence of silicon on iron containing smaller amounts of carbon. Incidentally he referred to the popular use of the phrase "specific gravity" as being highly objectionable: it was usually difficult to know what was meant. All ambiguity would be avoided if the density, *i.e.*, the weight of a cubic centimetre *in vacuo* at a specified temperature, were stated.

Mr. Turner said that he had not made any such experiments, but in a subsequent paper he hoped to show that Abel's experiments furnished information on the point in question.

65. "Modifications of Double Sulphates." By Spencer Umfreville Pickering, M.A.

The discordant statements as to the heat of dissolution of anhydrous potassium magnesium sulphate are due to the fact that it and its analogues exist in various distinct modifications.

The copper salt, $CuK_2(SO_4)_2,6H_2O$, on being dehydrated at any temperature between 100° and 130°, leaves a blue powder which dissolves in 800 molecules of water at 18·25°, with an evolution of 9709 cal. When this salt is further heated it loses its colour, becoming generally quite white, and then remains unaltered at any temperature below 250°. The second, or β-modification, dissolves with an evolution of only 6489 cal. at 18·25°. When heated above 250°, the white modification becomes blue again, and suffers no further change on raising the temperature till decomposition sets in at a few degrees above its melting point. This third or γ-modification dissolves in water with an evolution of 8407 cal. at 18·25°. The three modifications are all perfectly definite and stable compounds, with the slight exception that the white one does not attain a stable condition till about ten days after its preparation. When freshly prepared its heat of dissolution is 330 cal. less than it eventually becomes.

The sum of the heats of dissolution of copper sulphate and potassium sulphate at 18·25° is 9318 cal.: consequently no one of the three modifications consists of the constituent sulphates uncombined.

Potassium magnesium sulphate appears to undergo similar changes, but a dehydration at low temperatures is in this case a matter of difficulty; all specimens prepared between 110° and 155° gave identical numbers for the heat of dissolution at 22·28°, namely, 12,037 cal., corrections being applied where necessary for the small amount of water retained by the specimens. Above 155° the salt changes, dissolving with a smaller heat evolution as the temperature of its preparation is increased, till it reaches a minimum with the fused specimens, being then only 7431 cal. at 22·28°.

The fused salt dissolves with remarkable slowness; this observation leads to the suggestion that the insolubility of anhydrous alum is probably a consequence of some modification in its constitution similar to that experienced by the double magnesian sulphates.

66. "The Relation of Diazobenzene-anilide to Amidoazobenzene." By R. J. Friswell and A. G. Green.

Amidoazobenzene, an isomer of diazobenzene-anilide, is usually prepared by allowing the latter body to remain in contact with aniline hydrochloride in solution either in aniline, which is the most usual process, or occasionally in alcohol.

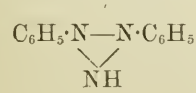
The change has been considered by Kekulé and others to be due to a double decomposition, but according to Griess, who discovered both bodies, the anilide is formed at a low temperature by the action of nitrous gas upon aniline, and the amido-compound by the same reagent at a high temperature.

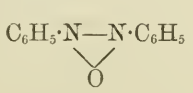
The authors have endeavoured to obtain amidoazobenzene directly from aniline or its salts, but no matter how the experiments were varied as to temperature, acidity, concentration, solvent, order of mixture, and mass of reacting materials, they found that diazobenzene-anilide was formed first, even where, being in the presence of a quantity of aniline salt and in a hot solution, it rapidly changed into the amido-azo-compound.

They have discovered that treatment of diazobenzene-anilide with weak chlorhydric acid causes the change, even in the absence of aniline hydrochloride; but they have also found that both this acid and dilute nitric acid have the power of resolving the anilide into diazobenzene and aniline chlorides; and they have observed that such mixtures by lapse of time combined again into amidoazobenzene, though if the acid were neutralised so as to cause a quick union the anilide was regenerated. From these and other facts detailed in the paper, it is inferred that neither is the isomeric change a double decomposition, nor is it due to a coercive action of the acid tending to the development of a basic from an indifferent body, strong acids such as oxalic and sulphuric being unable to produce the change. On the other hand, all the evidence points to *time* as being absolutely essential for the rearrangement of the molecule. At the same time, they are unable at present to account for the remarkable fact that amidoazobenzene can only result from a second stage reaction. It is apparently *necessary* for the union to take place, so as to form the anilide; this body having been formed, slowly decomposes into diazobenzene and aniline, which then *slowly* only react, forming amido-azobenzene. If their reunion is hastened the anilide is simply reformed.

The resolution of the anilide and the presence of the products in the solution account for the various decomposition products noticed as accompanying the formation of amidoazobenzene.

A similar isomeric change produced by an acid has been described by Wallach and Belli in the transformation of azoxybenzene into oxy-azobenzene by means of sulphuric acid. This change the authors think will probably prove to be analogous to the one now discussed, and agreeing with V. Meyer's opinion as to the necessity for a symmetrical formula for diazobenzene-anilide, they think that one formed on the type of the azoxybenzene formula to be open to little or no objection, thus:





67. "An Examination of the Phenol Constituents of Blast Furnace Tar obtained by the Alexander and McCosh Process at the Gartsherrie Iron Works." By Watson Smith, J. F. H. Coutts and H. E. Brothers. Part I.

By agitating the lighter creosote oils of the blast furnace tar with an equal bulk of caustic soda solution of 1·09 sp. gr., &c., the authors have obtained 17·5 per cent. by volume of crude phenols; while from ordinary gas retort tar, and also from Jameson coke oven oil, they have obtained about 5 per cent. However, by more exhaustive treatment with more concentrated soda solution, 23·1 per cent. of phenols was obtained from the blast furnace oil, and about 8 per cent. from the Jameson oil, which seems to be a nearer approach to the shale oil of the paraffin manufacturer; similarly, some 9 or 10 per cent. could be obtained from gas retort coal tar oil.

On fractioning the crude phenols from the blast furnace oil, only 5·63 per cent. by volume distilled over between 180° and 210°, 30·7 per cent. between 210° and 240°, and 18 per cent. between 260° and 300°. During the distillation of the portions boiling below 300°, and especially of the lower boiling portions, much sulphuretted hydrogen was evolved, and afterwards sulphurous oxide; at the same time a considerable amount of sulphur was deposited in the condenser. In fractioning the portion distilling from 300° to the coking point of the residue, when the latter point was reached both hydrogen cyanide and ammonia were evolved.

The phenols having been separated into groups boiling between certain temperatures, and these fractions purified as far as possible, they were distilled over heated zinc-dust: the hydrocarbons metaxylene, trimethylbenzene (probably pseudocumene), and naphthalene were thus obtained, and from their formation the authors infer the presence of the corresponding phenols in the original oils. Phenol itself was separated in small quantity from the portion distilling between 180° and 210°, metacresol being the chief constituent of this fraction; metaxylenol was one of the most abundant constituents of the portion boiling between 210° and 240°.

Inasmuch as low temperature tars such as that examined contain extremely little phenol, whereas gas retort tars are comparatively rich in this body and also in benzene, and also because other homologous phenols are so abundantly present in blast furnace tars, it is difficult to accept Schulze's theory as exclusively sufficient to account for so much benzene as is found in gas retort tars. According to this theory, in the formation of aromatic hydrocarbons by the destructive distillation of coal, phenols are primarily formed, and subsequently suffer disruption at higher temperatures, yielding water and aromatic

hydrocarbons. This may be the case to some extent, but it is likely that the synthetic reactions indicated in the theories of Berthelot, Jacobsen and Anschütz are also largely concerned in the production of the benzene, naphthalene, anthracene, &c.

68. "The Decomposition of Potassium Chlorate by Heat." By Frank L. Teed, D.Sc., F.C.S.

By heating potassium chlorate till it had lost varying amounts of oxygen, determining that oxygen from the loss in weight, and determining the potassium chloride produced by means of a decinormal silver nitrate solution, using potassium chromate as indicator, the author has come to the conclusion that potassium chlorate decomposes according to the equation $10KClO_3 = 6KClO_4 + 4KCl + 3O_2$.

The equation indicates that for every 74·5 parts of potassium chloride produced, there should be 24 parts of oxygen evolved; also that when potassium chlorate shall have yielded 7·84 per cent. of oxygen, all the chlorate is decomposed and nothing but perchlorate and chloride left.

The equation $2KClO_3 = KClO_4 + KCl + O_2$, by which the decomposition is ordinarily expressed, requires 32 parts of oxygen to every 74·5 of potassium chloride, and would not be complete till 13·06 per cent. of oxygen had been evolved.

The following are results obtained:—

Amount of $KClO_3$ taken. Grams.	Oxygen lost, per cent.	Potassium chloride formed, per cent.	Amount of oxygen to 74·5 of KCl.
3·2515	1·66	5·26	23·51
1·592	3·49	10·86	23·94
2·1725	6·00	18·25	24·49
3·956	10·52	27·36	28·65

The last experiment, in which 10·52 per cent. of oxygen was evolved, shows a much larger yield of oxygen to the 74·5 parts of potassium chloride, which is readily explainable by reference to the equation proposed. As mentioned above, the change represented by the equation is finished when 7·84 per cent. of oxygen is evolved, and 24·34 per cent. potassium chloride is produced.

The remaining 2·68 per cent. of oxygen can only be produced by the decomposition of potassium perchlorate in accordance with the equation $KClO_4 = KCl + 2O_2$; from this it follows that 74·5 parts potassium chloride are produced for every 64 of oxygen, and hence

that the evolution of 2·68 of oxygen should be accompanied by the formation of 3·14 of potassium chloride. Therefore, 10·52 of oxygen requires 24·34 + 3·14 = 27·48 of potassium chloride, a number agreeing fairly well with that found—27·36.

On treating some of the residue from the fourth experiment with sulphuric acid, only the faintest possible indication of a chlorate was obtained.

The author confirms the statement that no perchlorate is formed when potassium chlorate is heated with manganese binoxide, having found in one experiment—the only one made—a ratio of 74·5 of potassium chloride to 47·15 of oxygen (theory requiring 48), when the amount of oxygen evolved was only 3·38 per cent.

If potassium perchlorate be required in quantity, it would be considerably better to heat the chlorate till only 7·84 per cent. than till 13 per cent. of oxygen is evolved, as the equation $2KClO_3 = KClO_4 + KCl + O_2$ indicates a yield of 56·53 per cent. of perchlorate; the equation $10KClO_3 = 6KClO_4 + 4KCl + 3O_2$, a yield of 67·84 per cent.

Discussion.

Dr. Armstrong inquired whether any special method of heating had been adopted, and whether there was any evidence to prove that no perchlorate underwent decomposition in the first three experiments. Granting the correctness of the author's conclusions, the results were of interest, not only because they would enable us to correctly represent the decomposition of potassium chlorate, but also on account of the indication they appeared to afford that the molecular weight of the salt was much higher than is indicated by the formula $KClO_3$.

Dr. Teed replied that he had merely used a small flame in effecting the decomposition, and that he had no special proof to offer that the perchlorate had escaped decomposition. It had also occurred to him that his results might be regarded as evidence that potassium chlorate had a higher molecular weight.

69. "Note on the Refractive Power of Metacinname (Metastyrole)." By H. G. Madan, M.A., F.C.S.

A very full investigation into the properties of cinnamene was made by Blyth and Hofmann in 1845 (*Chem. Soc. Memoirs*, **2**, 334). They determined its index of refraction to be 1·532 for red rays, and observed its change into a polymer, metacinnamene, by being heated for a short time to a temperature of about 200° in a sealed tube. This latter substance they mention as having a higher refrac-

tive index than most organic substances, and as likely to be applicable for various optical purposes.

Scharling (*Annalen*, **97**, 187) made some further observations on both cinnamene and metacinnamene, and gives as the index of refraction of the latter body (or rather, of much thickened cinnamene) 1·464 for yellow rays; remarking that, though its density is greater than that of cinnamene, its refractive power is lower, contrary to the usual law.

In consequence of a suggestion kindly made by Dr. Perkin, that metacinnamene might be useful as a cement for direct-vision prisms and polarising prisms, the author has thought it worth while to examine the correctness of Scharling's determination of its refractive power.

In the first place, he determined the index of pure cinnamene, b. p. 144°. It was placed in a hollow prism (refracting angle 59° 48′) and the angle of minimum deviation for yellow monochromatic (sodium) light was found to be 40° 48′ 5″. From these data the index of refraction was found by the usual formula to be 1·541, which sufficiently corresponds with that given by Blyth and Hofmann for what is rather indefinitely called red light.

Some of the cinnamene was then placed in a tube, sealed up, and heated to 194—196° in an oil-bath for an hour. This was sufficient to transform it completely into a transparent, colourless, glass-like solid, which in the process of conversion contracted greatly, a hollow more than 1 cm. deep being formed in its surface, besides another vacuous space lower down in the tube.

When the tube was broken away from the metacinnamene, the latter appeared very like a rod of glass, but slightly flexible and not elastic, soft enough to be cut with a knife, though with difficulty. It became viscous when moderately heated, and seemed to bear sufficient heat to render it semi-fluid without being reconverted into normal cinnamene. Its density was determined to be 1·0563 (the density of pure metacinnamene is stated to be 1·054).

Some of the substance was melted, at as low a temperature as possible, into a hollow prism (brass with sides of plate glass, selected parallel) having a refracting angle of 51° 7′. The angle of minimum deviation from sodium rays was then determined to be 35° 44′ 35″; and hence the index of refraction for rays of wave-length 0·000588 mm. is 1·593. This is the mean result of two measurements, agreeing to the third decimal place.

The author is unable to account for the discrepancy between this value and the one given by Scharling, viz., 1·464 for what are rather indefinitely called "yellow rays." His specimen of metacinnamene probably contained unaltered cinnamene, but the index is even lower

than that of the latter substance. The presumption is in favour of a higher refractive power for a denser polymer.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

United States Geological Survey:

Monographs, Washington, 4to.

IV. Comstock Mining and Miners; by Eliot Lord, 1883:

V. Copper-bearing Rocks of Lake Superior; by R. D. Irving, 1883:

VI. Contributions to the Knowledge of the Older Mesozoic Flora of Virginia; by W. M. Fontaine, 1883:

VII. Silver-Lead Deposits of Eureka, Nevada; by J. S. Curtis, 1884. Bulletins 2—6; by J. S. Curtis:

VIII. Paleontology of the Eureka District; by C. D. Walcott, 1884: from the Director.

Smithsonian Contributions to Knowledge, vols. xxiv, xxv; 4to, Washington, 1885: from the Institution.

Early Proceedings of the American Philosophical Society for the Promotion of Useful Knowledge; compiled by one of the Secretaries from the Minutes of its Meetings from 1744—1838:

Philadelphia, 1884.

Report of the Director of the Mint (U.S.) upon the Production of the Precious Metals in the United States during the year 1884:

Washington, 1885.

Chemical Equilibrium, the Result of the Dissipation of Energy; by G. D. Liveing, Cambridge, 1885: from the Author.

Organic Chemistry; by Ira Remsen, Boston, 1885:

from the Author.

Papers on Technical Education, on Applied Science Buildings and their Fittings, and on Sanitation; by E. C. Robins: 4to, London, 1885.

New Theories of Matter and of Force; by W. Barlow, London, 1885: from Messrs. Sampson Low, Marston, Searle, and Rivington.

Familiar Lessons on Food and Nutrition; by T. Twining, London, 1882: from the Author.

Review of Agricultural Experiments, containing Criticisms and Suggestions; by T. D. Acland, London, 1885: from the Author.

Catalogue of the Library of the Linnean Society, London, Part I, Separate Works and Papers, 1866; Part II, Transactions of Societies,

Journals, and Supplement to Part I, 1867; Part III, Additions from 1866—1876, 1877: from the Society.

Photography with Emulsions: a Treatise on the Theory and Practical Working of the Collodion and Gelatine Emulsion Processes; by W. de W. Abney, London, 1885: from the Author.

Cambridge Philosophical Society. Transactions, vols. viii, ix, x, and xi, Parts I and II. Proceedings, vols. i and ii, Parts I—VI and XI—XVII: from the Society.

Royal Dublin Society. Transactions, vol. i, Parts X, XI, and XII; vol. ii, pages 137—180. Proceedings, New Series, vol. ii, Parts V and VI: from the Society.

Royal Cornwall Polytechnic Society. Annual Reports, 1833–36, 1838–50, 1852–54, 1856–58, 1863, and 1865: from the Society.

Glasgow Philosophical Society. Proceedings, vols. ii and iii, Parts IV, V, and VI; vols. iv and vi, Parts I and II:

from the Society.

Catalogo da Exposição Medica Brasileira realizada pela Bibliotheca de Faculdade de Medicina do Rio de Janeiro a 2 de Decembro de 1884; Rio de Janeiro, 1884: from the Author, Dr. Carlos Costa.

II. *By Purchase.*

Micro-Chemistry of Poisons; by T. G. Wormley, Philadelphia, 1885.

Quantitative chemische Analyse durch Electrolyse; von. A Classen, Berlin, 1885.

Traité de Pharmacie; par E. Souberain et J. Regnauld. Tome premier, Paris, 1885.

Introduction a l'étude de la Chimie; par A. Wurtz, Paris, 1885.

Acetonurie et Diaceturie; von R. v. Jaksch, Berlin, 1885.

Weitere Untersuchungen über Ptomaïne; von L. Brieger, Berlin, 1885.

A Treatise on the Principles of Chemistry; by M. M. Pattison-Muir, Cambridge, 1884.

Microscopische Reactionen: eine Einleitung zur Erkennung verschiedener Elemente unter dem Mikroscop; von Haushofer, Braunschweig 1885.

Anleitung zur Untersuchung der für die Zucker-Industrie in Betracht-kommenden, Rohmaterialien, Producte, Nebenproducte, und Hülfssubstanzen; von R. Frühling und J. Schulz, 3te Aufl., Braunschweig 1885.

Das Licht im Dienste wissenschaftlicher Forschung; von S. T. Stein, 2te Aufl., Hefte 1—3; Halle, 1885.

RESEARCH FUND.

A meeting of the Research Fund Committee will be held in December. Fellows desiring grants are requested to make application before December 5th.

NOTICE TO AUTHORS OF PAPERS.

To facilitate the preparation of these "Abstracts of Proceedings," all authors are requested to furnish abstracts of their communications, and to send their papers so that they may be in the hands of the Secretaries, if possible, on the Monday before the day of meeting.

At the next meeting, on November 19th, there will be a Ballot for the election of Fellows, and the following papers will be read:—

"Aluminium Alcohols. Part III. Aluminium Orthocresylate and its Products of Decomposition by Heat." By Dr. Gladstone and Mr. Tribe.

"Notes on the Constitution of Hydrated and Double Salts." By S. U. Pickering.

"On some Vanadium Compounds." By J. T. Brierley.

HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY, ST. MARTIN'S LANE.

ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 13. Session 1885-86.

November 19th, 1885. Dr. Hugo Müller, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. Robert G. Christopher, 35, Chantler Road, Custom House, Victoria Docks; William J. Cousins, 12, Maude Grove, West Brompton, S.W.; Andrew Thomson, 3, Viewforth Place, Dundee; William Watson Will, Ossory Villa, Ossory Road, S.E.; William Matthew Wilson, Bedford Cottage, Harpenden.

The following were elected Fellows of the Society:—Messrs. William James Bell, B.A.; Gibson Dyson; William Herbert Hyatt; Albert Ivatt; Gerald Martin; Thomas J. Menzies; Edward de Sonza; J. Dominie Vieira; Herman T. Vulté, Ph.B.; Ernest William Wiltshire; Arthur Benjamin Winstone; T. G. Wormley; James C. Wright.

The following papers were read:—

70. "Aluminium Alcohols. Part III. Aluminium Orthocresylate and its Products of Decomposition by Heat." By J. H. Gladstone, F.R.S., and Alfred Tribe.

Aluminium para- and metacresylate and their products of decomposition by heat have been previously described by the authors. They now give an account of the preparation of aluminium orthocresylate. As obtained, it consisted of a black vitreous mass, readily soluble in benzene, and decomposed by water.

The distillate obtained by heating it in a flask fitted with a wide bent tube was divided by fractionation into three portions: (*a*) boiling between 140° and 200°, (*b*) boiling between 200° and 300°, and (*c*) boiling above 300°. Fraction *a* was found to consist almost wholly of

the original substance. From fraction *b* a body was obtained which is shown to have the molecular formula $C_{14}H_{14}O$. From the properties and mode of formation of this body, it is concluded that it is orthocresylic ether, thus completing the series of ethers corresponding to the three isomeric cresols. From fraction *c* a small quantity was isolated of a body crystallising in diamond and star-shaped plates, and of a composition agreeing with the formula $C_{15}H_{14}O$. From the general properties and mode of formation of this body, the conclusion is drawn that it is isomeric with the "ketones" previously described.

The isomeric cresylates furnish very different amounts of distillate and of "ketone":—

	Distillate from 1000 parts.	Solid from 1000 parts.
Aluminium paracresylate ..	609	106
Aluminium metacresylate ..	640	20
Aluminium orthocresylate ..	475	2·5

The temperatures at which the destructive distillation of the several aluminium cresylates takes place are very different, this being more especially noticeable in the case of the para- and ortho-modifications. Besides probably accounting for the difference in the amounts of product obtained, this observation is of interest as showing that a difference exists in the stability of these aluminium isomerides.

71. "Notes on the Constitution of Hydrated and Double Salts." By Spencer U. Pickering.

Various attempts have been made to examine the differences in the individual molecules of water in a hydrated salt, amongst which Thomsen's determination of their heat of combination stands pre-eminent. The difference of the heat of dissolution of two hydrates such as $MgSO_4,3H_2O$ and $MgSO_4,4H_2O$ was assumed by him to give the heat of combination of the 4th water molecule, and so on; this is based on what the author believes to be a groundless assumption that the three molecules already combined are not in any way influenced by the addition of the fourth molecule: it would be as rational, he thinks, to argue that the energy with which an atom of lead is combined with one of sulphur in PbS remains unaltered after the absorption of oxygen to form lead sulphate. We have no reason for assuming that the energy with which several molecules cling together is not influenced by the addition of a fresh one, nor have we as yet any grounds for assuming that all the various water molecules in a hydrated salt are not precisely similar. The few arguments which may be brought to bear on the question all favour the opposite view.

The fact that one molecule of water in the magnesian sulphates is retained at a higher temperature than the others is no more a reason for regarding it as differing, either in nature or degree, from the rest than would the retention of one atom of oxygen in hydrogen dioxide at a much higher temperature than the other be a reason for regarding the two oxygen-atoms in this compound to be differently combined. The constitutional molecule theory has no *raison d'être*.

The accurate reproduction of the characteristics of copper and magnesium sulphates in the double salts which they form with potassium sulphate would lead to the conclusion that they are simple displacement products, $MgSO_4,K_2SO_4,6H_2O$ being similar to $MgSO_4,7H_2O$—so-called molecular compounds. This view is favoured by the fact that the specific heat of the anhydrous α-copper salt—that one which is obtained from the hydrated salt at the lowest possible temperature—is very nearly equal to the sum of the specific heats of the component sulphates, just as the specific heat of a hydrated salt is equal to the sum of the specific heats of the anhydrous salt and solid water.

The determinations gave—

α-$CuK_2(SO_4)_2$ molec. sp. heat	56·025
β- ,, ,, ,, ...	51·240
γ- ,, ,, ,, ...	58·735
$CuSO_4 + K_2SO_4$,, ,, ...	54·460

the last being somewhat low owing to experimental difficulties. As heat is developed in the passage of the α- into either the β- or γ-modifications, it is probable that the elements constituting these are more intimately combined than they are in the α-modification.

Although the heat of combination of $CuSO_4 + K_2SO_4$ is much smaller than $CuSO_4 + H_2O$, when the fully hydrated salts are considered it is seen that the double salt in crystallising out will evolve a larger amount of heat than the two sulphates would separately.

The tendency, as measured by the heat developed, of the α- to pass into the β-modification increases, and of the α- to pass into the γ-modification decreases, with the temperature. The formation of the γ-modification, therefore, as the temperature is raised, with an absorption of heat, is a good instance of the insufficiency of Berthelot's principle of maximum work to explain all chemical reactions.

Discussion.

Professor Ramsay said that it would perhaps be worth while to repeat Hannay's experiments on the rate at which water was lost by hydrated salts. He believed that Hannay had found that the rate was fairly constant as long as water of a certain kind was given off, and

changed when water of another kind was expelled. It would be interesting to know whether the $6H_2O$ in the double sulphates was lost at the same rate as the $6H_2O$ in magnesium sulphate.

Mr. Pickering replied that he had carefully studied Hannay's work and had corresponded with him. The breaks referred to were not well defined; in fact, he thought the experiments did not afford any very definite evidence.

72. "Some New Vanadium Compounds." By J. T. Brierley.

If a blue solution of hypovanadic sulphate be mixed with a colourless solution of an alkaline metavanadate, a dark-green liquid results, and if a slight excess of sodium hydroxide be added to this, the colour quickly changes to a deep black. Well-defined crystalline salts, having a purple or dark-green colour and metallic lustre, can be obtained from this dark solution. The following five are described:—

1. $2V_2O_4{\cdot}V_2O_5{\cdot}2Na_2O{\cdot}13H_2O$, soluble.
2. $2V_2O_4{\cdot}V_2O_5{\cdot}2K_2O{\cdot}6H_2O$, soluble.
3. $2V_2O_4{\cdot}4V_2O_5{\cdot}5K_2O{\cdot}H_2O$, insoluble.
4. $2V_2O_4{\cdot}2V_2O_5{\cdot}(NH_4)_2O{\cdot}14H_2O$, soluble.
5. $2V_2O_4{\cdot}4V_2O_5{\cdot}3[(NH_4)_2O]{\cdot}6H_2O$, insoluble.

By gently igniting the ammonium salt No. 5, a dark-green oxide is obtained, which readily absorbs moisture from the air, forming the hydrate $3(V_2O_4{\cdot}V_2O_5){\cdot}8H_2O$.

When the black oxide V_2O_3 is allowed to stand exposed to the air for many months, it absorbs oxygen and moisture, its colour changing to a light grass-green: analysis of such a product gave results agreeing with the formula $V_2O_4{\cdot}2V_2O_5{\cdot}8H_2O$; it dissolved in dilute sulphuric acid, and on neutralising the solution with potassium hydroxide and heating, the insoluble potassium salt No. 3 was obtained.

73. "On the Action of PCl_5 upon Ethylic Diethylacetoacetate." By J. W. James.

Geuther has shown that when ethylic acetoacetate is heated with PCl_5, ethoxyl becomes displaced by chlorine, two isomeric chlorocrotonic chlorides being formed. Rücker obtained a similar result with ethylic *methyl*acetocetate, the product being a single methylchlorocrotonic chloride. The author finds that ethylic *diethyl*acetoacetate behaves differently, the chief products being a mono- and a di-chlorinated derivative; what appears to be an ethylchlorocrotonic chloride is also formed in small quantity.

The diethylmonochlor- and dichlor-acetoacetates are converted into

corresponding *methoxy-* derivatives on careful treatment with sodium methoxide. If an excess of methoxide be employed, the diethylmethoxyacetoacetate is converted into methylethylmethoxyacetone, $CH_2(OMe)\cdot CO\cdot CHEtMe$, a somewhat abnormal decomposition.

Ethylic diethyldimethoxyacetate behaves normally in presence of excess of methoxide, and is converted into diethyldimethoxyacetone, $CH(OMe)_2\cdot CO\cdot CHEt_2$.

Ethylic diethylacetoacetate is not acted upon by aqueous ammonia at 120—130°, and at 190—200° is converted into diethylacetone: its behaviour in this respect is therefore also different from that of ethylic acetoacetate.

74. "On the Vapour-pressures of Mercury." By W. Ramsay, Ph.D., and Sydney Young, D.Sc.

After criticising Regnault's determinations of the vapour-pressures of mercury, the authors show that his results do not agree with the following generalisation, which has been proved to be true in twenty-two instances.

A relation exists between the absolute temperatures of all bodies, whether solid or liquid, whether stable or dissociable, which may be expressed in the case of any two bodies by the equation

$$R' = R + c(t' - t),$$

where R is the ratio of the absolute temperatures of the two bodies corresponding to any vapour-pressure, the same for both; R′ is the ratio at any other pressure, again the same for both; c is a constant which may equal 0, or a small plus or minus number; and t' and t are the temperatures, absolute or centigrade, of one of the bodies corresponding to the two vapour-pressures. When $c = 0$, $R' = R$, or the ratio of the absolute temperatures is a constant at all pressures; and when $c > 0$ or $c < 0$, its values may readily be determined either by calculation, or graphically by representing the absolute temperatures of one of the two bodies as ordinates, and the ratios of the absolute temperatures at pressures corresponding to the absolute temperatures of that body as abscissæ. It is found in all cases that points representing the relation of the ratio of the absolute temperatures of the two bodies to the absolute temperatures of one of them lie in a straight line.

From this it follows that if the vapour-pressures of any one substance are known throughout, it is sufficient to determine accurately the vapour-pressures of any other substance at any two temperatures, sufficiently far apart, in order to be able to construct its whole vapour-pressure curve.

The vapour-pressures of mercury have accordingly been measured

with the greatest care at the temperatures:—222·15° C., 270·3°, 280·2°, 447°, and 448°.

On comparing the ratios of the absolute temperatures of mercury and water, at pressures corresponding to those temperatures, they are found to agree with the equation $R' = R + c(t - t')$, where $c = 0{\cdot}0004788$, if the temperatures of mercury be chosen as ordinates.

It is therefore possible to construct the complete vapour-pressure curve of mercury; the paper contains tabular statements of the values.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Wilson's Inorganic Chemistry: revised and enlarged; by H. G. Madan, London and Edinburgh, 1885: from the Editor.

Lectures on Heat, Sound, and Light; by R. Wormell, London, 1885: from the Publisher.

Chemical Students' Manual for the Lecture Room and Laboratory; by H. C. Buckeridge, London, 1885: from the Publisher.

II. *By Purchase.*

The British Pharmacopœia; London, 1885.

A Guide to the New Pharmacopœia (1885); by P. James, London, 1885.

Handbook of Technical Gas-analysis; by C. Winkler. Translated with a few additions by G. Lunge; London, 1885.

A Text Book of the Principles of Physics; by A. Daniell, 2nd edition; London, 1885.

A Manual of Practical Analysis; by G. S. W. Wills, 8th edition; London, 1885.

Physico-chemical Constants; Melting and Boiling Point Tables; by T. Carnelley, vol. i; London, 1885.

Titles of Papers of interest to Chemists recently read before Societies in the United Kingdom:—

"On the Velocity with which Air rushes into a Vacuum, and on some Phenomena attending the Discharge of Atmospheres of higher into Atmospheres of lower Density." By Henry Wilde.

Manchester Literary and Philosophical Society, October 28th.

"On testing Thermometers at the Melting-point of Mercury." By G. M. Whipple.

Physical Society, November 14th.

Opening Address of the Chairman of the Society of Arts, Sir F. A. Abel. November 18th.

"On Dissociation and Evaporation." Part I. By Professors Ramsay and Young.

Royal Society of London, November 19th.

SALE OF THE "ABSTRACTS OF PROCEEDINGS."

The Council have resolved to place the "Abstracts of Proceedings" on sale at the beginning of the new year at a price of *7s. 6d.* per annum. Intending subscribers and fellows who desire to purchase extra copies are requested to apply to Mr. Van Voorst, Paternoster Row, London, E.C.

RESEARCH FUND.

A meeting of the Research Fund Committee will be held in December. Fellows desiring grants are requested to make application before December 5th.

NOTICE TO AUTHORS OF PAPERS.

To facilitate the preparation of these "Abstracts of Proceedings," all authors are requested to furnish abstracts of their communications, and to send their papers so that they may be in the hands of the Secretaries, if possible, on the Monday before the day of meeting.

RECEPTION OF FELLOWS.

A Reception will be held by the President and Council at 8 o'clock on the evening of December 13th. Fellows are requested to exhibit objects of interest to chemists. Morning dress.

At the next meeting on December 3rd, there will be a ballot for the election of Fellows, and the following papers will be read :—

"The Sugars of the Cereals, and in Malted Grain."

"On the presence of 'Raffinose' in Barley."

By C. O'Sullivan, F.R.S.

"On the Evidence of Constitution afforded by Absorption Spectra."

By Captain Abney, F.R.S.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 14. Session 1885-86.

December 3rd, 1885. Dr. Hugo Müller, F.R.S., President, in the Chair.

The following were formally admitted Fellows of the Society:—Messrs. Herbert C. Lea, Arthur Winstone, Ernest W. Wiltshire.

Certificates were read for the first time in favour of Messrs. Peter MacEwan, 36, York Place, Edinburgh; Andrew Henderson, 29, Merchiston Park, Edinburgh; William Lang, Jun., Cross Park, Partick, N.B.; Arthur Pillans Laurie, Nairne Lodge, Duddingstone, N.B.; Walter Newton, Park Green, Macclesfield; Francis Napier Sutton, 150, Loughboro' Road, S.W.; Claude Metford Thompson, University College, Cardiff; Julius Wertheimer, Oxford Terrace, St. Helens, Lancashire.

The following were elected Fellows of the Society:—Messrs. Richard Haliburton Adie; John Sabin Adriance, M.A.; Charles Morton Aikman; James Anderson; Edward Brown Clark; Malcolm J. R. Dunstan; George E. R. Ellis; James Epps, Jun.; Lazarus Fletcher; William L. Gadd; Gilbert Prout Girdwood; William H. Greene, M.D.; Ernest William Harvey; George Hirst; Thomas Holgate; Matthew Hunter, B.A.; George H. Hurst; John Cecil Husband; Lewis Gordon Paul, Ph.D.; Leonard Peckitt; Charles Ranken; Luther R. Scammell; James Sim; Henry J. Staples; Stephen Stephenson; Henry Stoker; Edward E. H. Thorn; Thomas B. Tyson; Henry Collins Williams; Charles Francis Young.

The following papers were read:

75. "On the Presence of 'Raffinose' in Barley." By C. O'Sullivan, F.R.S.

If the alcoholic extract of barley be evaporated and the syrup dis-

solved in the least possible quantity of alcohol, and a little ether added, crystals are obtained which after recrystallisation form flattened rhombic prisms terminated by a dome parallel to the shorter axis.

The composition of these crystals is represented by the formula $C_{18}H_{32}O_{16}{\cdot}5H_2O$. They melt in a little water, but are not very soluble in strong alcohol. The substance does not reduce an alkaline cupric solution. The optical activity of the anhydrous body is $[\alpha]_j = +135$; it is slowly inverted by invertase, but rapidly by a 1 per cent. solution of sulphuric acid; the product of inversion readily reduces an alkaline cupric solution. It is fermented by ordinary yeast. With nitric acid it yields mucic, oxalic and saccharic acids.

76. "On the Sugars of some of the Cereals and of Germinated Grain." By C. O'Sullivan, F.R.S.

Barley and wheat are proved to contain sucrose and other non-reducing and reducing fermentable sugars, the nature of which was not accurately determined. Germinated barley contains an increased quantity of sucrose, also maltose, dextrose and lævulose. The following table is given to show the change that takes place during germination, the results being calculated in percentages on the dry matter of the body, the yield of dry malt from dry barley being known:—

	No. 1 Barley.		No. 2 Barley.	
	Before germination.	After germination.	Before germination.	After germination.
Sucrose	0·9	4·5	1·39	4·5
Maltose	1·1	1·2	0·62	1·98
Dextrose		3·1		1·57
Lævulose		0·2		0·71

In highly malted barley the sucrose is high, or if not its place is taken by the products of its inversion. Maltose also is high in highly malted grain, but occasionally its place is taken by dextrose.

With wheat the results are similar.

As high as 11·4 per cent. sucrose, calculated on the solid matter, has been found in unfermented, unacted-upon malt-wort.

Discussion.

Mr. Banister expressed his indebtedness to the author. From

experiments made on cereals in their laboratory in 1880, he was able to confirm Mr. O'Sullivan's conclusions as to the presence of sucrose in them. The results obtained were published in the second part of the South Kensington Art Handbook on the Analysis and Adulteration of Foods, page 86. A table is there given of the quantity of sugar found in certain cereals, but as this sugar was not isolated, and only examined chemically and optically, it was said of it on page 87 of the same book, that "The saccharine body behaves like cane-sugar on being inverted with the same facility, and in not reducing a solution of copper salt." Other references are made to this sugar in different parts of the book, and as it was not crystallised out, it would not have been proper to call it cane-sugar, although it possessed all its properties. The amount of the sugar in the cereals examined was determined; the results were as follows:—

Wheat, winter sown	2·57 per cent.
Wheat, spring sown	2·24 ,,
Barley, long-eared	1·34 ,,
Oats, English	2·36 ,,
Maize	1·94 ,,
Rye	4·30 ,,
Rice, Carolina.....	0·38 ,,

The quantity of sugar present in the rye is very remarkable, and especially so as it was found that the samples of rye examined contained no sugar having a reducing action upon copper, while in all the others there was a dextrose body present in greater or less proportion.

In 1871 they had to make a series of experiments on malt worts and the changes wrought in them by the addition of different quantities of cane-sugar. During that inquiry evidence was obtained that there was a saccharine substance in malt possessing most of the properties of cane-sugar, and the results then recorded were worked out on the same lines as we now use for expressing copper reducing power, &c., and accord closely with the most recent observations on the subject.

Mr. O'Sullivan, replying to Mr. Salamon, said that the method employed by him in estimating sucrose excluded albuminoïds, and his analysis therefore did not afford any information as to whether such compounds were present in amounts varying with the sucrose and maltose. Dextrin or malto-dextrin was certainly present, but in very small amount, in malted grain. He added that the peculiarities in rye were probably largely due to the fact that it was usually cut green, and therefore contained bodies which were not fully elaborated.

77. "Atomic Valency." By S. U. Pickering.

The ordinary theory of atomic valency, though it may lead to many inconsistencies, must nevertheless be regarded as expressing many undeniable facts; that it is imperfect, however, must be admitted, if only on the ground that it takes no cognisance of the existence of that large class of bodies known as "molecular compounds." These cannot be satisfactorily explained, either by assuming oxygen to be a tetrad, or by the supposition of a "molecular" attraction comparable with the atomic attraction which gives rise to atomic compounds. Theoretical as well as experimental considerations indicate that the relations of the various atoms in a molecule are altered by the combination of that molecule with another to form a molecular compound; this has led the author to refer the formation of such compounds to peculiarities in the valency of the individual atoms. He considers that the number which represents the valency of any atom, though it may very nearly approach to a whole number, is not exactly a whole number, but is slightly greater or smaller than such.

The double sulphates, which for many reasons may be considered as typical molecular compounds, consist of a sulphate, such as the alkali-metal sulphates, which do not form either hydrated or basic compounds, united with a sulphate of the magnesium or aluminium class, which form both hydrated and basic compounds. A basic salt would appear to be due to the fact that one equivalent of the metallic oxide is insufficient to saturate one equivalent of the acid; conversely, in a salt which does not form a basic salt, the acid or electro-negative portion of the normal salt will either exactly saturate, or more than saturate the positive portion. Since in the former class of salts the excess of valency possessed by the negative portion is saturated by combination with a further quantity of the metallic oxide, these oxides must be regarded as possessing what may for brevity sake be termed an excess of positive valency. Water will be included in these metallic oxides, and will consequently act like them; a salt which forms basic salts will therefore form hydrated salts, and one which does not form basic salts will be anhydrous; this is nearly always the case.

Taking the valency of H to be 1, that of O may be represented by some number slightly less than 2, say 1·98, water will then be represented as $(H_2^{\cdot}O^{1\cdot98})^{+\cdot02}$, (using Arabic numerals to represent the valency, preceded by a sign indicating to which portion of the compound the excess of valency is due), a compound sufficiently saturated to be stable, but yet capable of further saturation, such as might be produced by its combination with any molecule exhibiting a slight

excess of negative valency. The magnesian sulphates would be represented as being such bodies, *e.g.*,

$$[Mg^{1\cdot99}(SO_4)^{2\cdot135}]^{-0\cdot145},\ [Zn^{1\cdot989}(SO_4)^{2\cdot135}]^{-0\cdot146},$$

whereas a sulphate such as potassium sulphate would contain an excess of positive valency, thus—

$$[(K_2)^{2\cdot159}(SO_4)^{2\cdot135}]^{+0\cdot024},$$

the former class would become more saturated by the addition of water,

$$[(MgSO_4)^{-0\cdot145}(7H_2O)^{+0\cdot14}]^{-0\cdot005}$$
$$[(ZnSO_4)^{-1\cdot45}(7H_2O)^{+0\cdot14}]^{-0\cdot006},$$

and still more so by the displacement of one of the water molecules by a molecule of potassium sulphate—

$$[(MgSO_4)^{-0\cdot145}(K_2SO_4)^{+0\cdot024}(6H_2O)^{+0\cdot12}]^{-0\cdot001}.$$

It would be possible, however, for such double salts as this, as well as for the heptahydrated magnesian sulphates, to combine with each other, but even if the residual valency in any two of these was of opposite sign it would be comparatively very small, and the double salts so formed would be much less well defined than the potassium-magnesium sulphates, or the alums. An investigation of these bodies has proved that such is in reality the case; although the double salts

$$[MgSO_4{\cdot}7H_2O,CuSO_4{\cdot}7H_2O],\text{ and}$$
$$[MgK_2(SO_4)_2{\cdot}6H_2O,CuK_2(SO_4)_2{\cdot}6H_2O],$$

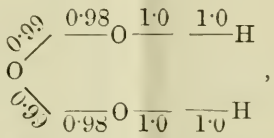
can scarcely be regarded as simple mixtures, they are certainly not definite compounds.

Lithium sulphate, being hydrated, should not form double salts, like potassium sulphate; and neither with the magnesium nor the aluminium sulphates does it produce such compounds. Sodium sulphate is undoubtedly exceptional.

The fundamental idea of this theory of unequivalent valencies is that each valency is to a certain extent divisible: the valency of K_2 in K_2SO_4 is represented as not only saturating that of the SO_4 in its own molecule, but of aiding the saturation of the SO_4 in another molecule, $MgSO_4$. Applying this idea to atomic compounds, it will be seen that whereas water is an unsaturated compound, hydrogen dioxide may be saturated,

$$\begin{array}{l} \overset{0\cdot98}{|}\ O\overset{1\cdot0}{\text{———}}\ \overset{1\cdot0}{\text{———}}H \\ \\ \overset{0\cdot98}{|}\ O\overset{1\cdot0}{\text{———}}\ \overset{1\cdot0}{\text{———}}H \end{array},$$

the two valencies of oxygen assuming different values. This will give some explanation of the possibility of the formation of such a body, though, from the presence in it of what may be termed asymmetric oxygen atoms, its stability would not be great. H_2O_3, however, would probably be incapable of existence, for it would not only contain asymmetric atoms, but would also be an unsaturated compound, thus—



and, as a matter of fact, neither it nor any corresponding compound of a monad metal does exist. But there would not be the same objections to the existence of H_2O_3, for it would form a saturated compound, and, although such an oxide of hydrogen is unknown, the corresponding potassium oxide exists.

The objections to the existence of oxides of monad metals containing 3 or 5 atoms of oxygen would not apply to their sulphides, for the higher valency of sulphur would permit of such a compound as H_2S_3 being saturated, consequently we find that such sulphides do exist.

The author proceeds to show that, in some cases, a slight increase of complexity may favour stability, whereas, in others, it would produce the reverse effect. As instances of the former he takes Cu_2S_2, As_4O_6, S_2O_6: he also shows that a metal which is in reality a tetrad may never occur in any but a pseudotriad form, as in the case of aluminium. His theory, he considers, gives also a clear conception of why the properties of one atom are affected, not only by the nature of another atom with which it is combined, but also by the nature and number of the other atoms to which this second one is united.

Finally he suggests that the peculiarities of the compounds of carbon and hydrogen may receive some explanation from such a theory. It is only necessary to imagine that the valency of hydrogen is exactly, or very nearly exactly, equivalent to each valency of carbon, and we have at once an explanation of the possibility of producing compounds of these elements far more complex than those of any other elements. If such be the case, it will follow that the hydrocarbons will show little or no tendency to form molecular or residuary compounds, and, as a matter of fact, the number of such compounds which they form is very small when compared with those of other bodies. The introduction of oxygen into a hydrocarbon will not endue it with a tendency to form a true hydrate, for the resulting body will possess an excess of positive atomicity, consequently we find that the com-

pounds of water with an oxygenated hydrocarbon are more correctly represented as "atomic" compounds (hydrols), and that it is only on the introduction of some element other than oxygen, that a substance is obtained capable of forming a true hydrate.

ADDITIONS TO THE LIBRARY.

I. *Donation.*

Études de dynamique chimique; par J. H. Van't Hoff. Amsterdam, 1884: from Leonard de Koningh, Esq.

II. *By Purchase.*

Commercial Organic Analysis; by A. H. Allen; 2nd edition; vol. i; London, 1885.

Gorup-Besanez' Lehrbuch der Chemie; 7te Auflage, neu bearbeitet von A. Rau. Band I. Anorganische Chemie; Braunschweig, 1885.

Handbuch der pharmaceutischen Praxis; von H. Hager; Neue Ausgabe, Lieferung i; Berlin, 1885.

Vereinbarungen betreffs der Untersuchung und Beurteilung von Nahrungs- und Genussmitteln, sowie Gebrauchsgegenständen. Herausgegeben, im Auftrage der freien Vereinigung bayerischer Vertreter der angewandten Chemie; von A. Hilger; Berlin, 1885.

Mikroskopie der Nahrungs- und Genussmittel aus dem Pflanzenreiche; von J. Moeller; Berlin, 1885.

Titles of Papers of interest to Chemists recently read before Societies in the United Kingdom:—

"Studies of Disinfectants by New Methods." By A. Wynter Blyth.

"Researches on Myohæmatin and the Histohæmatins." By Dr. C. A. MacMunn.

Royal Society of London, November 26th.

"On the Necessity for a National Standardising Laboratory for Electrical Instruments." By Dr. J. A. Fleming.

Society of Telegraph Engineers and Electricians, November 26th.

"On the Calibration of Galvanometers by a Constant Current." By T. Mather. Physical Society, November 28th.

SALE OF THE "ABSTRACTS OF PROCEEDINGS."

The Council have resolved to place the "Abstracts of Proceedings" on sale at the beginning of the new year at a price of *7s. 6d.* per annum. Intending subscribers and fellows who desire to purchase extra copies are requested to apply to Mr. Van Voorst, Paternoster Row, London, E.C.

NOTICE TO AUTHORS OF PAPERS.

To facilitate the preparation of these "Abstracts of Proceedings," all authors are requested to furnish abstracts of their communications, and to send their papers so that they may be in the hands of the Secretaries, if possible, on the Monday before the day of meeting.

RECEPTION OF FELLOWS.

A Reception will be held by the President and Council at 8 o'clock on the evening of December 10th. Morning dress.

At the next meeting on December 17th, there will be a ballot for the election of Fellows, and the following papers will be read:—

"The Action of Steam on Carbonic Oxide." By H. B. Dixon.

"On Multiple Sulphates." By Miss E. Aston and S. U. Pickering.

HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY, ST. MARTIN'S LANE.

ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 15. Session 1885-86.

December 17th, 1885. Dr. Hugo Müller, F.R.S., President, in the Chair.

Messrs. W. Dalrymple Borland, James Epps, jun., Lazarus Fletcher, and Lewis Gordon Paul, were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Henry Kelway George Bamber, 5, Westminster Chambers, S.W.; Adolph Dressel, 1, Marlow Road, Anerley, S.E.; Herbert Samuel Ebworthy, Rosa, North West Provinces, India; Bertram Harvey Hart, The Elms, Old Charlton, Kent; George Thomas Holloway, 17, Bridge Road, West Battersea; Eugene Obach, 2, Victoria Road, Old Charlton, Kent; Oliver Quibell, Highfield, Newark; Richard Spencer, Holker Street, Barrow-in-Furness.

The following were elected Fellows of the Society: Messrs. Robert G. Christopher, William J. Cousins, Andrew Thomson, William Watson Will, William Matthew Wilson.

The following circular letter was read by the Secretary:—

ELIZABETH THOMPSON SCIENCE FUND.

This fund, which has been established by Mrs. Elizabeth Thompson, of Stamford, Connecticut, "for the advancement and prosecution of scientific research in its broadest sense, now amounts to $25,000. As the income is already available, the trustees desire to receive applications for appropriations in aid of scientific work. This endowment is not for the benefit of any one department of science, but it is the intention of the trustees to give the preference to those investigations, *not already otherwise provided for*, which have for their

object the advancement of human knowledge, or the benefit of mankind in general, rather than to researches directed to the solution of questions of merely local importance.

Applications for assistance from this fund should be accompanied by a full statement of the nature of the investigation, of the conditions under which it is to be prosecuted, and of the manner in which the appropriation asked for is to be expended. The applications should be forwarded to the Secretary of the Board of Trustees, Dr. C. S. Minot, 25, Mt. Vernon Street, Boston, Mass., U. S. A.

The first grant will probably be made early in January, 1886.

(Signed) H. P. Bowditch, *President.*
Wm. Minot, Jr., *Treasurer.*
Francis A. Walker.
Edw. C. Pickering.
Charles Sedgwick Minot, *Secretary.*

The following papers were read:

78. "The Action of Steam on Carbonic Oxide." By H. B. Dixon.

The action of steam in determining the union of carbonic oxide and oxygen has been explained by the author as leading to an alternate reduction and oxidation whereby the hydrogen conveys the oxygen to the carbonic oxide:—(1) $CO + H_2O = CO_2 + H_2$; (2) $2H_2 + O_2 = 2H_2O$. This explanation has been rejected by Moritz Traube (*Ber.*, 1885, p. 1890) on the ground that carbonic oxide does not decompose steam at a high temperature. Traube represents the influence of steam as consisting in the formation from it of peroxide of hydrogen, which oxidises carbonic oxide, steam being reformed.

The author has already shown that steam is decomposed by carbonic oxide at a high temperature, for when carbonic oxide is exploded in presence of steam with insufficient oxygen to completely burn it, the carbon dioxide formed is more than double the oxygen, and hydrogen is found in the residue. Horstmann arrived at the same conclusion.

When sparks are passed through a mixture of steam and carbonic oxide, carbon dioxide and hydrogen are formed until a certain fraction (which varies with the nature of the spark) of the carbonic oxide is turned into carbon dioxide.

When sparks are passed through a mixture of carbon dioxide and hydrogen, carbonic oxide and steam are formed until a certain fraction of the carbon dioxide is turned into carbonic oxide.

In neither case is the reaction complete. An equilibrium is reached when about 10 per cent. of carbon dioxide is present to 90 of carbonic oxide.

By the prolonged passage of the sparks a considerable quantity of formic acid is produced.

When a coil of platinum wire is heated to redness in steam and carbonic oxide, carbon dioxide and hydrogen are formed until from 10 to 15 per cent. of the carbonic oxide has been oxidised. Similarly, when a coil of platinum wire is heated in carbon dioxide and hydrogen, carbonic oxide and steam are formed until the corresponding limit is reached. No formic acid is produced. When a coil of wire is maintained at a red heat in a mixture of carbonic oxide and steam, and the carbon dioxide formed is removed by means of a dilute solution of potash, the carbonic oxide is in time completely oxidised to carbon dioxide with the liberation of the corresponding volume of hydrogen. Similarly, when a coil of platinum wire is maintained at a red heat in a mixture of carbon monoxide and hydrogen, and the steam formed is removed by means of phosphoric oxide, the carbon dioxide is in time completely reduced to carbonic oxide.

Since these experiments were made Naumann has shown that when carbonic oxide and steam are heated in a tube to 950°, 10·5 per cent. of carbonic oxide is turned into carbon dioxide.

79. "On Multiple Sulphates." By Miss E. Aston and S. U. Pickering.

Double salts of the type $M''SO_4{\cdot}K_2SO_4{\cdot}6H_2O$ are stated by Vohl to be capable of combining with each other in definite proportions, forming "double-, triple-, or quadruple-double sulphates."

By mixing the constituents in various proportions the authors have found that no definite salts can be obtained, but that a constant variation in the composition of the product results from a variation in the proportion of the salts taken. These results were obtained whether the solutions were mixed in the cold, whether hot solutions were allowed to crystallise by cooling, or whether the solutions were left to evaporate spontaneously.

The potassium-magnesium-copper sulphate and the potassium-cobalt-copper sulphate were the two salts belonging to the first-mentioned class which were examined. In the second class the cases examined were copper-magnesium sulphate and cobalt-magnesium sulphate. With the former of these there even appears to be a strong disinclination to crystallise in a proportion in any way approaching to an equal number of molecules of the constituent sulphates.

The only argument in favour of the existence of these salts must be that with those which contain potassium the copper salt carries down with it a certain quantity of the magnesium salt, even from a solution too dilute to yield this latter of its own accord; and, with those which

do not contain potassium, that an excess of either the copper or the magnesium sulphate will induce the other to crystallise out in a form and with a proportion of water foreign to its nature. That such salts, however, can be ranked with definite compounds is impossible.

Discussion.

Mr. J. M. Thomson agreed with Mr. Pickering that the salts in question were compounds of a very indefinite nature. In a paper published in the British Association Report for 1877, he, however, had pointed out that in the case of the double sulphates of potassium and nickel or cobalt, if the crystallisation take place spontaneously or at temperatures below 80°, a regular displacement of each other by the nickel and cobalt is observed: the water, SO_4, and potassium remaining constant in the several fractions. Instead, however, of the simple formula $(M''M'')K_4(SO_4)_4{\cdot}12H_2O$ given by Vohl, a much more complex formula, such as $24[M''M''K_4(SO_4)_4{\cdot}12H_2O]$, is required to express the relation between the two metals. The fractions are very distinctly dichroic, and when examined through the two opposite axes, a change of colour may be observed in successive fractions. This is also evidence of some state of association more definite than isomorphous mixture, as large crystals taken for analysis exhibited the same dichroism throughout.

80. "On the Use of Ferrous Sulphate in Agriculture." By A. B. Griffiths, Ph.D.

Wheat crops have been grown during the past season by the author with and without the addition of iron sulphate to the land ($\frac{1}{2}$ cwt. to the acre). The crop grown with iron sulphate yielded $32\frac{1}{2}$ bushels of grain, while that grown without yielded 30 bushels; hence it appears that iron sulphate is not such a good manure for cereals as for root and leguminous crops. On the other hand, a Mr. Edgson, of Etton, near Peterborough, has used iron sulphate with considerable benefit for wheat crops this year. It is stated that iron sulphate used as a top-dressing to grass-land destroys moss, and that the ashes of the dead moss contained 11·56 per cent. of iron oxide. The grass, on the other hand, grew well after the treatment, and the amount of ferric oxide in its ashes was only 2·46 per cent. It is also stated that a solution containing 0·1 gram of iron sulphate in 100 grams of water destroys *Peronospora infestans* and its spores; also the "wheat-mildew" and its spores.

In a series of experiments with potatoes, three plots of land of the same size were manured—B with iron sulphate and artificial manures,

C with the artificial manure alone, and plot A was left normal. B gave a yield of $8\frac{1}{2}$ tons of tubers, C, $6\frac{1}{2}$ tons, and A only 3 tons.

The best way to apply the sulphate to the land is as a top-dressing, the quantity being $\frac{1}{2}$ cwt. to the acre.

81. "On Phenyltribromomethane, $C_6H_5 \cdot CBr_3$." By Walter H. Ince.

The author describes a method of preparing this compound by adding bromine to boiling toluene in a specially constructed apparatus in which the use of corks and caoutchouc is avoided; he has also prepared it by passing the vapour of toluene into a flask filled with bromine vapour. It is a colourless, mobile liquid, soluble in alcohol, ether, benzene, and toluene; when heated above about 150° it decomposes, and cannot therefore be purified by distillation. It slowly decomposes on exposure to sunlight. Its vapour has a perfectly overpowering action on the eyes and mucous membranes. When heated with water it readily forms benzoic acid; but it is very slightly acted upon even after prolonged boiling with alcohol.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Journal and Proceedings of the Royal Society of New South Wales: Vol. 18: Sydney, 1885: from the Society.

Fourth Annual Report (1882-3) of the U. S. Geological Survey: 4to.: Washington, 1884. from the Director.

Annual Report of the Board of Regents of the Smithsonian Institution for the year 1883: Washington, 1885: from the Institution.

II. *By Purchase.*

Vorlesungen über Bacterien: von A. de Bary: Leipzig, 1885.

Report to the Trinity House on the Relative Merits of Electricity, Gas, and Oil, as Lighthouse Illuminants: folio: London, 1885.

Titles of Papers of interest to Chemists recently read before Societies in the United Kingdom:—

"On the Limited Hydration of Ammonium Carbonate." By H. J. Fenton, M.A.

"A Preliminary Account of a Research into the Nature of the

Venom of the Indian Cobra (*Naja Tripudians*)." By Dr. R. Norris Wolfenden.

"A New Form of Spectroscope." By J. Norman Lockyer, F.R.S. Royal Society of London, December 10th and 17th.

"On some Thermodynamical Relations." By Professors Ramsay and Young. Physical Society, December 17th.

SALE OF THE "ABSTRACTS OF PROCEEDINGS."

The Council have resolved to place the "Abstracts of Proceedings" on sale at the beginning of the new year at a price of 7*s.* 6*d.* per annum. Intending subscribers and fellows who desire to purchase extra copies are requested to apply without delay to Mr. Van Voorst, Paternoster Row, London, E.C.

At the meeting on February 4th, Dr. Klein, F.R.S., will deliver a lecture on "Methods of bacteriological research from a biologist's point of view."

HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY, ST. MARTIN'S LANE.

CHARTER

AND

BYE-LAWS

OF

THE CHEMICAL SOCIETY.

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1878.

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THE CHEMICAL SOCIETY.

ORIGIN AND FORMATION.

A MEETING, convened by Mr. Warington for the purpose of taking into consideration the formation of a Chemical Society, was held in the rooms of the Society of Arts, John-street, Adelphi, on February 23rd, 1841, at which the following gentlemen were present:—Arthur Aikin, Esq., Dr. Thos. Clark, W. J. Cock, Esq., J. T. Cooper, Esq., D. Cooper, Esq., Thos. Everitt, Esq., Wm. Ferguson, Esq., J. P. Gassiot, Esq., Thos. Graham, Esq., W. R. Grove, Esq., H. Hennell, Esq., T. H. Henry, Esq., C. Heisch, Esq., G. Lowe, Esq., W. H. Miller, Esq., Apsley Pellatt, Esq., Richard Phillips, Esq., Dr. Lyon Playfair, Robert Porrett, Esq., Dr. G. O. Rees, E. Solly, Jun., Esq., James Tennant, Esq., E. F. Teschemacher Esq., Dr. R. D. Thomson, and Robert Warington, Esq.

Professor Graham having been called to the Chair, it was unanimously resolved, "That it is expedient that a Chemical Society should be formed," and a Provisional Committee, consisting of Messrs. A. Aikin, W. T. Brande, H. J. Brooke, J. T. Cooper, Rev. J. Cumming, J. F. Daniell, T. Everitt, T. Graham, W. R. Grove, H. Hennell, G. Lowe, R. Phillips, R. Porrett, and R. Warington, was appointed to carry this resolution into effect.

The objects of the Society were defined to be—

> "The promotion of Chemistry and of those branches of Science immediately connected with it, by the reading, discussion, and subsequent publication, of original communications."

"Also the formation of a Chemical Library, and Museum."

"It was proposed that the Annual Subscription for Members resident within twenty miles of London, should be Two Pounds; beyond that distance, One Pound."

At the first General Meeting, held on the 30th of March, 1841, the Provisional Committee brought forward a Report, embodying a plan for the constitution and government of the Society. The Report, with some amendments, was adopted by the Meeting.

The following gentlemen were then elected as the first Officers and Council:—President—T. Graham, Esq.; Vice-Presidents—W. T. Brande, Esq., J. T. Cooper, Esq., J. F. Daniell, Esq., R. Phillips, Esq.; Treasurer—Arthur Aikin, Esq.; Secretaries—Robert Warington, Esq., E. F. Teschemacher, Esq.; Council—Dr. T. Clark, Rev. J. Cumming, M.A., Dr. C. Daubeny, T. Everitt, Esq., T. Griffiths, Esq., W. R. Grove, Esq., H. Hennell, Esq., G. Lowe, Esq., W. H. Miller, Esq., M.A., W. H. Pepys, Esq., R. Porrett, Esq., Dr. G. O. Rees. The names of seventy-seven gentlemen who had become Members were then read, and the Society adjourned until Tuesday, the 13th of April.

The Society continued to meet regularly, from time to time, and published Memoirs and Reports of their Proceedings, which at the close of the year 1847 amounted to three volumes.

As the Members of the Society at this time amounted to between 200 and 300, it appeared desirable that steps should be taken for obtaining a Charter of Incorporation; and, at the Anniversary Meeting for 1848, a Resolution was passed—

"That it be recommended to the Council for their consideration, whether it would be for the interests of the Society to procure a Charter of Incorporation."

In pursuance of this Resolution, the Council made the necessary inquiries, and a Special Meeting of the Society was summoned on the 22nd of May, 1848, to receive their Report, in which the Council advised the Society to make application to Government for a Charter. The Report was adopted by the Meeting, and it was resolved—

> "That this Meeting do authorise the Council to take the necessary steps for procuring a Charter of Incorporation."

Application was therefore made to the Government authorities in due form, and the Royal Assent having been obtained, the Society was incorporated under the following Charter.

CHARTER.

VICTORIA, by the Grace of God of the United Kingdom of Great Britain and Ireland, Queen, Defender of the Faith, to all to whom these presents shall come greeting. WHEREAS WILLIAM THOMAS BRANDE, of our Mint, Esquire, a Fellow of the Royal Society and of the University of London, and others of our loving subjects, did in the year 1841 establish, and are now Members of, a Society known by the name of the Chemical Society, for the general advancement of Chemical Science, as intimately connected with the prosperity of the manufactures of the United Kingdom, many of which mainly depend on the application of chemical principles and discoveries for their beneficial development, and for a more extended and economical application of the industrial resources and sanatory condition of the community: AND WHEREAS it has been farther represented to us that the same Society has, since its establishment, sedulously pursued such its proposed object, by holding meetings at stated periods, at which new discoveries have been brought under dis-

cussion, and the results made known to the public in a series of Transactions from time to time published by the said Society, and that distinguished individuals in foreign countries have availed themselves of the facilities offered by the same Society for communicating important scientific and practical discoveries made abroad, and that thus a useful interchange of valuable information has been effected: AND WHEREAS the same Society has hitherto been supported by donations and annual and other subscriptions and contributions to its funds, and has expended and continues to expend considerable sums of money in the publication of its Transactions, in aid of which objects a Library of scientific works, and also a Museum of chemical preparations and standard instruments are in course of being formed: AND WHEREAS, in order to secure the property of the said Society, and to extend its useful operations, and at the same time to give it a more permanent establishment among the scientific institutions of our kingdom, WE have been besought to grant to the said WILLIAM THOMAS BRANDE, and to those who now are or shall hereafter become Members of the said Society, our Royal Charter of Incorporation for the purposes aforesaid:—

NOW KNOW YE, that we being desirous of encouraging a design so laudable and salutary of our especial grace, certain knowledge, and mere motion, have willed, granted, and declared, and do by these presents, for us, our heirs and successors, will, grant, and declare, that the said WILLIAM THOMAS BRANDE, and such others of our loving subjects as now are Members of the said Society, or shall from time to time be elected Fellows thereof, according to such regulations or bye-laws as shall be hereafter framed or enacted, and their successors shall for ever hereafter be, by virtue of these presents, one body politic and corporate by the name of THE CHEMICAL SOCIETY, and for the purposes aforesaid and by the name aforesaid shall have perpetual succession

and a Common Seal, with full power and authority to alter, vary, break, and renew the same at their discretion, and by the same name to sue and be sued. implead and be impleaded, answer and be answered unto in every court of us, our heirs and successors, and be for ever able and capable in the law to purchase, receive, possess, hold, and enjoy, to them and their successors, any goods and chattels whatsoever; and also to be able and capable in the law (notwithstanding the statutes of mortmain) to take, purchase, possess, hold, and enjoy to them and their successors, a hall or house and any such messuages, lands, tenements, or hereditaments whatsoever, as may be necessary for carrying out the purposes of the Society, the yearly value of which, including the site of the said hall or house, shall not exceed in the whole the sum of £3,000, computing the same respectively at the rack-rent which might have been had or gotten for the same respectively at the time of the purchase or acquisition thereof; and to act in all the concerns of the said body politic and corporate for the purposes aforesaid, as fully and effectually to all intents, effects, constructions, and purposes whatsoever, as any other of our liege subjects or any other body politic in our United Kingdom of Great Britain and Ireland, not being under any disability, might do their respective concerns; AND WE DO HEREBY GRANT our especial licence and authority unto all and every person and persons, bodies politic and corporate otherwise com petent, to grant, sell, alien, and convey in mortmain. unto and to the use of the said body politic and corporate and their successors, any messuages, lands, tenements, or hereditaments, not exceeding such annual value as aforesaid:

AND OUR WILL AND PLEASURE IS, AND WE FURTHER GRANT AND DECLARE, that there shall be a General Meeting or General Meetings of the Fellows of the said Society, to be held from time to time as hereinafter mentioned, and that there shall be a Council to direct

and manage the concerns of the said body politic and corporate, and that the General Meetings and the Council shall have the entire direction and management of the same, in the manner and subject to the regulations hereinafter mentioned: BUT OUR WILL AND PLEASURE IS that at all General Meetings and Meetings of the Council the majority present and having a right to vote thereat respectively shall decide upon the matters propounded at such Meetings, the person presiding therein having, in case of an equality of numbers, a second or casting vote:

AND WE DO HEREBY ALSO WILL, GRANT, AND DECLARE, that there shall be a President, Vice-Presidents, a Treasurer and Secretaries of the said body politic and corporate, and that the Council shall consist of the President, Vice-Presidents, Treasurer, Secretaries, and not more than twelve nor less than eight other Fellows of the said Society; AND WE DO HEREBY FURTHER WILL AND DECLARE, that the said WILLIAM THOMAS BRANDE shall be the first PRESIDENT of the said body politic and corporate, and the other persons now being the Vice-Presidents, Treasurer, Secretaries, and other Members of the Council, shall be the first Members of the Council of the said body politic and corporate, and shall continue such until the election of Officers shall be made in pursuance of these presents:

AND WE DO HEREBY FURTHER WILL AND DECLARE, that it shall be lawful for the Fellows of the said body politic and corporate hereby established to hold a General Meeting once in the year or oftener, for the purposes hereinafter mentioned, namely, that the President, Vice-Presidents, the Treasurer, the Secretaries and other Members of the Council, shall be chosen at such General Meeting; and that the General Meetings shall from time to time make and establish such bye-laws as they shall deem to be useful and necessary for the regulation of the said body politic and corporate, for the admission of Fellows, the election of Associates,

and of Honorary and Foreign Members, and for the management of the estates, goods, and business of the said body politic and corporate, for fixing and determining the number of Vice-Presidents, Secretaries, and the number of the other Members of the Council as aforesaid, and the time and manner of electing the President, Vice-Presidents, Treasurer, Secretaries, and other Members of the Council, and the period of their respective continuance in office; and such bye-laws from time to time they shall or may alter, vary, or revoke, and shall or may make such new and other bye-laws as they shall think most useful and expedient for the said body politic and corporate, so that the same be not repugnant to these presents or to the laws and statutes of this our realm, and shall and may also enter into any resolution, and make any regulation respecting any of the affairs and concerns of the said body politic and corporate that shall be thought necessary and proper:

And we do further will and declare, that the first such General Meeting as aforesaid for the election of officers shall take place within twelve calendar months from the date of these presents, and that the present rules and regulations of the said Society, so far as they are not inconsistent with these presents, shall continue in force until the same shall be altered by a General Meeting:

And we further will, grant, and declare, that the Council shall have the sole management of the income and funds of the said body politic and corporate, and the appointment of an Assistant-Secretary, Librarian, Curator, and such other officers, attendants, and servants, as shall in the discretion of the Council be deemed necessary or useful for the said Society, as also the entire management and superintendence of all the other affairs and concerns thereof, and shall and may, but not inconsistent with or contrary to the provisions of this our Charter, or any existing bye-law, or laws and statutes of this our realm, do all such acts

and deeds as shall appear to them necessary or essential to be done for the purpose of carrying into effect the objects and views of the said body politic and corporate; PROVIDED ALWAYS, AND WE DO WILL AND DECLARE, that the Council shall from time to time render to a General Meeting a full and particular account of all such their proceedings as aforesaid, and that it shall be lawful for every Fellow of the said Society to see and examine the accounts of the receipts and payments of the said body politic and corporate:

AND WE FURTHER WILL, GRANT, AND DECLARE, that the whole property of the said body politic and corporate shall be vested, and we do hereby vest the same, solely and absolutely, in the Fellows thereof, and that they shall have full power and authority to sell, alienate, charge, and otherwise dispose of the same as they shall think proper; but that no sale, mortgage, incumbrance, or other disposition of any messuages, lands, tenements, or hereditaments belonging to the said body politic and corporate, shall be made, except with the approbation and concurrence of a General Meeting:

AND WE DO HEREBY FURTHER WILL AND DECLARE, that the service of the President, Vice-Presidents, Treasurer, Secretaries, and other Members of the Council, shall be honorary, and that it shall not be lawful for them, or any of them, to receive any pecuniary payment for their attendance or other services in or about the affairs of the said body politic and corporate, and that no dividend, gift, division, or bonus in money, shall be made out of the funds of the said body politic or corporate, unto or among any of its Fellows:

AND WE LASTLY DECLARE it to be our Royal will and pleasure, that no resolution or bye-law shall on any account or pretence whatsoever be made by the said body politic and corporate in opposition to the general scope, true intent and meaning of this our Charter, or the laws or statutes of our realm; and that if any such rule or bye-law shall be made, the same shall be absolutely null

and void to all intents, effects, constructions, and purposes whatsoever. In witness whereof we have caused these our Letters to be made Patent. Witness ourself at our Palace at Westminster, this Second day of November, in the 12th year of our Reign.

By Writ of Privy Seal,
EDMUNDS,

L. S.

In accordance with the preceding Royal Charter, the Chemical Society consists of Fellows, Honorary and Foreign Members and Associates.

The Fellows elect, out of their own body, according to the following Rules, a Council consisting of a President, four or more Vice-Presidents, a Treasurer, two Secretaries, a Foreign Secretary, and twelve other Fellows, by whom the business of the Society is conducted in conformity with the following bye-laws.

BYE-LAWS.

I.—*Of the Election, Admission, and Payments by Fellows.*

The method of voting for the election of Fellows shall be by ballot.

Every Candidate for election into the Society as a Fellow thereof shall be proposed according to a form of recommendation (see No. 1 Appendix) subscribed by not less than five Fellows of the Society, to three, at least, of whom he shall be personally known; and such certificate shall be read at three Ordinary Scientific Meetings, and be suspended in the Society's rooms or place of meeting until the Candidate has been duly balloted for.

Ballots shall take place at Ordinary Scientific Meetings, and those Candidates shall be balloted for whose

certificates have been read at two previous Ordinary Scientific Meetings, and again on the evening of the ballot.

The election shall not be valid unless forty or more Fellows vote; but if an insufficient number of votes be recorded, the particular Candidate or Candidates put up for ballot shall be again balloted for at the next Meeting or Meetings. When three-fourths or more of the Fellows who vote are in favour of the Candidate, he shall be elected a Fellow; but when less than three-fourths of the Fellows who vote are in favour of the Candidate, he shall not be elected a Fellow. The result of the ballot shall be ascertained by two Scrutators and one of the Secretaries, and declared by the Chairman.

The Fellow thus elected shall sign the following obligation, and return it to the Secretary:—"I, the undersigned, do hereby engage that I will endeavour to promote the interests and welfare of the Chemical Society; that I will observe its laws, and to the utmost of my power, maintain its dignity, as long as I shall continue a Fellow thereof." This obligation records his acquiescence in all the Rules, Regulations, and Laws of the Society, and pledges him to their due observance.

The formal admission of Fellows shall take place after the reading of the Minutes at Ordinary Scientific Meetings of the Society.—After the reading aloud by one of the officers of the prescribed form of obligation, the Fellow to be admitted shall subscribe his name to the obligation in the Charter-book, and be introduced to the Chairman, who, taking him by the hand, shall say:—"Mr. _____, I do, by the authority and in the name of the Chemical Society, admit you a Fellow thereof."

Every Fellow shall have the right to be present and to vote at all Meetings of the Society; and to propose Candidates for admission into the Society; and he shall be entitled, so long as his annual subscription be not one year in arrear, to one copy of the annual publications of

the Society. He shall also be entitled to the use of the instruments and books in the Society's collection, under such restrictions as the Council may deem necessary. He shall have the privilege of introducing two visitors to the Ordinary Scientific Meetings of the Society, whose names shall be entered in a book kept for that purpose, together with the name of the Fellow introducing such visitors.

Every Fellow, previous to his admission, shall, within three months from the date of his election, pay an admission fee of Four Pounds, and either his first annual subscription, or a life composition fee, otherwise his election shall be void; power to extend this period of three months being, however, reserved to the Council.

The annual subscription to be paid by Fellows shall be Two Pounds; excepting that those Fellows residing more than twenty miles from London, who shall have been elected before the first day of January, 1860, shall pay One Pound. The subscriptions of Fellows shall become due on the first day of January in every year.

If, however, a Candidate be elected during the month of November or December, he shall not be called upon to pay any annual subscription for the current year, and shall not be entitled to receive the publications of the Society for that year.

The life composition fee shall be Twenty Pounds, excepting that those Fellows residing more than twenty miles from London who shall have been elected before the first day of January, 1860, may compound by the payment of Ten Pounds.

II.—*Of Honorary and Foreign Members.*

Honorary and Foreign Members shall be recommended to the Society by the Council. They shall be nominated at one Meeting of the Council, and shall be balloted for at some subsequent Meeting of the Council,

and if the majority of those voting are in favour of any Candidate, he shall be proposed by the Council to the Society at a subsequent Ordinary Scientific Meeting, and be balloted for at the Ordinary Scientific Meeting of the Society following that at which he was recommended for election according to the Rules for the election of Fellows.

The number of Honorary and Foreign Members shall not exceed forty. The Honorary and Foreign Members shall not be required to contribute to the Funds of the Society. Each shall receive a copy of the annual publications of the Society.

III.—*Of Associates.*

Associates shall be recommended to the Society by the Council, and shall be balloted for in the same manner as Fellows. They shall be elected under the same conditions, but for a period of three years only, at the expiration of which time they may be again recommended for election.

Associates shall pay an annual subscription of One Pound. They shall have the ordinary privileges of Fellows, but shall neither vote in the Society nor propose Fellows, nor shall they be entitled to a gratuitous copy of the annual publications of the Society, but they shall have the option of paying an annual subscription of Thirty shillings in place of One Pound, for which higher subscription they shall be entitled to a copy of the Society's Journal, in addition to the ordinary privileges of Fellows, with the exceptions hereinbefore specified.

IV.—*Withdrawing and Removal of Fellows and Associates.*

Any Fellow who at the period of the Annual General Meeting of the Society in March shall have left his subscriptions unpaid for two years, reckoning from the

1st of January preceding, such subscrpitions having been applied for by Circular No. 4 in the Appendix, and no reason satisfactory to the President and Council having been assigned for their nonpayment, shall cease to be a Fellow of the Society, and have his name removed from the Society's List accordingly: Provided, nevertheless, that on a solicitation for re-admission being addressed to the President and Council by a person so circumstanced, the case of such person shall be considered by the Council, who may, if they see fit, reinstate him as a Fellow of the Society, upon his paying up the arrears of his subscription, or a life composition fee.

Any proposition to remove a Fellow or Associate from the Society, for other causes than the nonpayment of subscriptions, must be made by the Council. It shall be read at any Ordinary Scientific Meeting of the Society, and at the like Meeting next ensuing the proposition shall be balloted for, and if three-fourths of the Fellows voting shall vote for the removal of such Fellow or Associate, he shall be removed from the Society accordingly.

The ballot shall not be valid unless forty or more persons vote.

V.—*Election of President, Officers, and Council.*

All Officers of the Society shall be elected by ballot at the Annual General Meeting, in March.

At the second Ordinary Scientific Meeting, in February, the Chairman shall declare: 1st. The names of the two Vice-Presidents who it is proposed should retire, either from the Council, or, in the event of one of them being nominated to the Presidency, from the Vice-Presidency. 2nd. The names of four ordinary Members of the Council who it is proposed should also retire. 3rd. The names of the President and officers recommended for election to office during the ensuing

year, including the names of two new Vice-Presidents selected either from the existing Council, or from the general body of Fellows. 4th. The names of four new ordinary Members, recommended for election to the Council, or in the event of two ordinary Members of Council being nominated to the Vice-Presidency, of six new Members, or in the event of one ordinary Member of Council being nominated to the Vice-Presidency, of five new Members.

Two lists, according to the forms Nos. 5 and 6 in the Appendix, with the names of the Fellows recommended for election as official and ordinary Members of Council, and having each a blank column opposite for such alterations as any Fellow may wish to make, shall be prepared by the Secretaries. These two lists shall be read from the Chair at the first Ordinary Scientific Meeting in March, and, on or before the day of meeting, shall be suspended in the Society's rooms and circulated among the Fellows.

In the event of any Fellow proposing some other name or names than those recommended by the Council, and communicating his proposal in writing, duly signed by himself, to one of the Secretaries before the second meeting in March, the same shall be read from the Chair, and be publicly suspended in the Society's rooms with the list recommended by the Council.

On the day of Election, two Scrutators shall be nominated by the Chairman, with the approbation of the Meeting, to assist the Secretaries in examining the lists. Each Fellow voting shall deliver his list to one of the Scrutators, and the name of the Fellow so voting shall be recorded by one of the Secretaries. The names of those reported to the Chairman by the Scrutators as having the majority of votes of the Fellows present, for filling the offices of President, Vice-Presidents, Treasurer, Secretaries, and Council, shall then be announced from the Chair as elected to serve for the ensuing year.

In the event of votes being recorded for the same Candidate, both as an Officer and as a Member of Council, the votes recorded for him as an Officer shall, in the case of his not being elected an Officer, be added to those recorded for him as a Member of Council, and the total number of votes shall be counted as votes for the Council.

VI.—*Of the President.*

The President shall preside at the Meetings of the Society and of the Council, and shall regulate the order of the proceedings.

No Fellow shall be elected as President of the Society for more than two years in succession, but he may be re-elected after the lapse of one year.

In case of a casual vacancy the Council shall name a Vice-President to exercise the powers and perform the duties of President.

VII.—*Of the Vice-Presidents.*

In the absence of the President, the Chair shall be occupied by one of the Vice-Presidents, or, in the absence of any Vice-President, by a Member of Council or some other Fellow.

Fellows who have filled the office of President at any time since the formation of the Society, shall be proposed by the Council for election as Vice-Presidents, and this proposition shall be renewed every year, excepting when any such Vice-President is again nominated to the Presidency. There shall be six other Vice-Presidents who have not filled the office of President, of whom two shall retire from the Council every year, unless one of the outgoing Vice-Presidents be nominated to the Presidency, when only one other Vice-President shall retire.

VIII. *Of the Treasurer.*

The Treasurer shall receive all money due to the Society, and shall pay such sums as may be ordered by the Council. He shall keep an account of such receipts and payments, in which donations and money received for composition of annual payments shall be entered separately from the ordinary revenues of the Society, and he shall produce such account at any Meeting of the Council, when required.

The Treasurer shall pay the moneys received by him into the hands of the Society's banker, retaining a sum not exceeding £100 for the payment of current expenses.

The Treasurer shall, on the first day of January annually, send to every Fellow of the Society who has not compounded for his annual contribution, a printed copy of the Intimation contained in No. 3 in the Appendix; and in making up his Accounts in the month of March of every year for the examination of the Auditors, he shall present a list of all Fellows whose subscriptions are then in arrear.

At the second Ordinary Scientific Meeting of the Society in February, three Auditors shall be elected by the Society by show of hands, unless a ballot be demanded. They shall audit the Treasurer's Account, and shall forward their Report to the Council at least one week before the Annual General Meeting of the Society. They shall have the power of calling for all necessary accounts and vouchers. No Member of the Council shall be eligible as an Auditor.

IX.—*Of the Secretaries.*

There shall be two Secretaries and a Foreign Secretary. The duties of the Secretaries shall be—1st. To attend, one or both, at all Meetings of the Society and of the Council. 2nd. To take Minutes of the proceedings,

and to read them at the ensuing Meeting. 3rd. To read all Scientific Communications to the Society, or abstracts thereof, that are not read by their respective authors. 4th. To address to every person elected into the Society a printed copy of the Letter No. 2 in the Appendix, and of the Obligation, together with a copy of the Bye-Laws of the Society, a List of the Fellows, and a Card announcing the days on which the Society holds its Meetings during the Session. 5th. To prepare and circulate the Balloting Lists of the Council. 6th. To conduct the home correspondence of the Society. A book shall be kept in the charge of the Secretaries, containing a copy of the Charter and Laws of the Society, with the form of Obligation to be subscribed by each Fellow. The several duties to be performed by each Secretary to be arranged by the Council.

The Foreign Secretary shall conduct the foreign correspondence of the Society.

X.—*Of the Council.*

The business of the Society shall be conducted by a Council, consisting of the President, the Vice-Presidents, the Treasurer, the Secretaries, and twelve other Fellows, not fewer than eight of whom shall, at the time of election, be resident within twenty miles of London. Annually four of the twelve ordinary Members of Council (three at least of whom must be resident Members) shall retire from the Council, and four new Members shall be elected to supply their places. At all Meetings of the Council five shall be a quorum.

The Council shall hold their Ordinary Meetings at least once a month, from November to June inclusive, on one of the days of the Ordinary Scientific Meetings of the Society. Notice of the time of holding each Meeting of the Council shall be forwarded by one of the Secretaries to each Member of the Council at least two

days previous to that on which such Meeting is to be held, but the non-receipt of such notice by any Member of the Council shall in no way invalidate the proceedings of the Meeting.

Extraordinary Meetings of the Council shall be called by the President upon a requisition to him, signed by three Members of the Council, or at his own discretion, when he shall direct the Secretaries to issue summonses for the occasion.

The ordinary mode of decision on questions before the Council shall be by show of hands, unless a ballot be demanded. Any Member of the Council who shall be personally concerned in the question under consideration, shall retire during the discussion and determining of the same.

At the Annual General Meeting, the President shall present a Report on the state of the Society during the past twelve months.

Before any new Bye-Law, or alteration of the existing Bye-Laws, be brought before the Society by the Council, it shall be proposed at one Meeting of the Council, and considered and approved of at a subsequent Meeting.

The Council shall have the power of appointing and of removing the Assistant Secretary, Librarian, Curator, or other paid Officers of the Society.

XI.—*Ordinary Scientific Meetings of the Society.*

The Ordinary Scientific Meetings of the Society shall be held twice in every month, from November to June inclusive, except in the month of January, when the Society shall meet once only; the specific days and hours of meeting to be determined by the Council. The ordinary course of business shall be as follows, subject, however, to the control of the Chairman for the time being:—1st. The names of the Visitors, and of the Fellows by whom they are introduced, shall be an-

nounced from the Chair. 2nd. The Minutes of the proceedings of the previous Meeting shall be read and submitted for confirmation. 3rd. New Fellows shall sign the obligation book, and shall be admitted by the Chairman. 4th. Presents made to the Society since its last Meeting shall be announced from the Chair. 5th. The certificates of Candidates for election shall be read. 6th. Scientific communications shall be read and discussed. 7th. The titles of papers ordered for reading at the next Meeting shall be announced.

XII.—*Annual General Meeting.*

An Annual General Meeting of the Society shall be held on the 30th day of March, at eight o'clock P.M. (or on such day in March near that time as the Council may determine), for the election of Officers and Council for the year ensuing, and for receiving the Report of the President on the state of the Society.

Notice of the Annual General Meeting shall be given from the Chair, at the two preceding Ordinary Scientific Meetings of the Society, and also upon the lists of the Ordinary Meetings which are forwarded to the Fellows.

XIII.—*Extraordinary Meetings of the Society.*

An Extraordinary General Meeting of the Society shall be summoned at any time by the President, on his receiving a written requisition to do so from the Council, or from twenty Fellows of the Society. Notice shall be given of such Meeting at a previous Ordinary Scientific Meeting, or by a circular addressed to all the resident Fellows. The President shall have the power of calling an Extraordinary General Meeting.

XIV.—*Of the Reading and Publication of Scientific Papers.*

The Secretary shall mark upon each paper sent to him, the date on which he received it from the author, and also the date upon which it was read to the Society. These papers shall, as far as expedient, be read in the order in which they are received, and the discussion of each paper shall immediately follow the reading thereof, unless the Chairman for the time being shall otherwise direct. The discussion of any paper may, on a resolution of the meeting to that effect, be resumed at the following Meeting. Authors may read their own papers, by permission of the Chairman.

All papers communicated to the Society, with their illustrative Drawings, shall become the property of the Society, unless stipulation be made to the contrary; and authors shall not be at liberty, save by permission of the Council, to publish in English the papers they have communicated, until such papers, or abstracts of them, have either appeared in the Journal of the Society, or have been returned to the author.

The Journal of the Society shall be published at intervals to be determined by the Council. It shall consist of such of the papers which have been read at the Meetings of the Society, or of abstracts of them, as the Council may determine, together with abstracts of papers published in other Journals.

If any paper of importance is communicated during the recess, the same may be ordered for publication by the Council, without being read to the Society.

The authors of such papers as may be published by the Society shall be entitled to fifty copies of each of their own papers, free of expense.

XV.—*Library.*

The books in the possession of the Society shall be allowed to circulate among the Fellows and Associates, under such regulations, and with such exceptions as the Council may deem advisable.

XVI.—*Common Seal and Deeds.*

The Common Seal of the Society shall remain in the custody of the President. Every Deed or Writing to which the Common Seal is to be affixed, shall be passed and sealed in Council.

APPENDIX.

No. 1.

CHEMICAL SOCIETY.

Certificate of a Candidate for Election.

Name_____

Usual Place of Residence_____

Designation or Occupation_____

Qualifications.*

_____

_____

_____

_____

being desirous of admission into the CHEMICAL SOCIETY, *we, the undersigned, propose and recommend him as a proper person to become a* FELLOW *thereof.*

*Dated this*_____*day of*_____18

From Personal Knowledge.	From General Knowledge.

Proposed on _____

*To be Balloted for on*_____

*Elected*_____18

_____

President.

* Directions for filling up the Certificate are given on the other side.

Directions for filling up the Certificate of a Candidate.

Under "Qualifications" should be given a concise statement of the Candidate's contributions to Chemical Science, as Investigator or Author, or of his position and past experience as Lecturer, Teacher, Assistant or Student, or in connection with Analytical or Manufacturing Chemistry.

If the Candidate's qualifications are not included under any of the above heads, the reasons for his desiring admission to the Society should be stated.

The Certificate must be signed by *five* or more Fellows, of whom *at least three* must certify their recommendation from *personal* knowledge.

No. 2.

Letter notifying the Election of a Member.

Sir,

I have the honour to inform you, that on the day of you were elected a Fellow of the Chemical Society. I herewith transmit you a copy of the Bye-laws, &c

According to the Regulations of the Society, you are required to return the accompanying Obligation, duly signed, to the Secretary, and to pay the Collector, the Admission Fee of £4, and the Annual Contribution for the current year, £2, before admission.*

I have the honour to remain,

Your obedient Servant,

Secretary.

* In the case of Honorary Members, Foreign Members, and Associates, this paragraph will be omitted.

No. 3.

Annual Circular Letter of Treasurer.

January 1, 18

Sir,

I have the honour to inform you that your Annual Contribution of £_____ to the Chemical Society for the year _____, is due.

If paid by Post-Office Order, it should be drawn on the Post-office, London, made payable to the Collector, and enclosed to him (_____
_____).

I have the honour to be,

Your obedient Servant,

_____ *Treasurer*

No. 4.

Annual Circular Letter of the Treasurer to Fellows who are two years in arrear of their Subscriptions.

January 1, 18

Sir,

I have to inform you that your Subscription of £2 to the Chemical Society for the current year is now due, and that you are also in arrear of your subscription for the two preceding years _____ and _____.

I have also to inform you that, if your arrears, amounting to £4, are not paid on or before the 30th of March next ensuing, you will, in accordance with the

IVth Bye-law, cease to be a Fellow of the Society, and your name will be struck off from the list.

Payments can be made by Cheque or by Post-office Order, drawn on the Post-office, London, in favour of the Collector, , Burlington House, Piccadilly.

I am, Sir,

Your obedient Servant,

_____ *Treasurer.*

[*Issued by authority of the Council.*]

No. 5.

Balloting List for the Election of President and Officers.

CHEMICAL SOCIETY.

March, 18

BALLOTING LIST

FOR THE ELECTION OF OFFICERS.

Present Officers.	*Officers Proposed.*	
PRESIDENT.		
VICE-PRESIDENTS.		
SECRETARIES.		
FOREIGN SECRETARY.		
TREASURER.		

If you wish to substitute any other name, in place of that proposed, erase the printed name in the second column, and write opposite to it, in the third, that which you wish to substitute.

[*Issued by authority of the Council.*]

No. 6.

Balloting List for the Election of Ordinary Members of Council.

CHEMICAL SOCIETY.

BALLOTING LIST.

March, 18

FOR THE ELECTION OF ORDINARY MEMBERS OF COUNCIL.

Present Members.	*Names of Fellows proposed.*	

If you wish to substitute any other name, in place of that proposed, erase the printed name in the second column, and write opposite to it, in the third, that which you wish to substitute.

A

CATALOGUE

OF

THE LIBRARY

OF

THE CHEMICAL SOCIETY.

LONDON:
HARRISON AND SONS, ST. MARTIN'S LANE.
Printers in Ordinary to Her Majesty.

1874.

REGULATIONS.

1. The Library is open for consultation and for the issue and return of books, daily, between the hours of 10 and 5, and on Monday and Thursday evenings, from 7 to 9.

2. No books are issued without a voucher, to be left with the officer in attendance.

3. Members are not allowed to have more than Six volumes at a time from the Library, without special permission obtained from the Librarian, nor to retain a book for a longer time than fourteen days. But when a book is returned by a Fellow, it may be borrowed by him again, provided it has not been bespoken by any other Fellow. Books which have been bespoken shall circulate in rotation, according to priority of application.

4. THE SCIENTIFIC JOURNALS ARE NOT TO BE CIRCULATED UNTIL THE VOLUMES ARE COMPLETED AND BOUND.

5. Fellows retaining books longer than the time specified shall be subject to a fine of Sixpence per week for each volume.

6. The books which have been issued shall be called in by the Librarian twice a year, and in the event of any book not being returned on such occasion, the Fellow to whom it was last issued shall be answerable for it, and may be required to replace it if lost.

CATALOGUE.

Abel and Bloxam. Handbook of Chemistry, Theoretical, Practical, and Technical. 8vo. London, 1854.

Academia (Real) de Ciencias de Madrid: Memorias. 4to. 3ª Serie. Tomos 1—6. (1850–1863).

——— Resumen de las Actas. 8vo. 1850–1, 1851–2, and 1852–3.

Academy of Natural Sciences of Philadelphia: Proceedings, 8vo. Philadelphia.

Vol. VII. (1855). Nos. 8, 9, 10, 11, 12.
VIII. (1856).
IX. (1857).
X. (1858).
Vol. XI. (1859). Nos. 1 to 20, and 24 to 27.
(1862). Nos. 7 to 12.
(1863), (1864).
(1868—1872).

Accademia delle Scienze dell' Istituto di Bologna: Memorie. 4to.

Tomo VII.—1856.
,, VIII.—1857–8.
,, IX.—1859.
,, X.—1860.
,, XI.—1861.
,, XII.—1862.

2me Série.

,, I.—1862.
,, II.—1862.
,, III.—1863.
,, IV.—1864–65.

Tomo V.—1865–66.
,, VI.—1866.
,, VII.—1867.
,, VIII.—1868.
,, IX.—1869.
,, X.—1870.

3ª Série.

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,, II.—1872.
,, III.—1873

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——— Indici generali, 1850–1861. 4to. Bologna, 1864.

——— Rendiconti. 8vo. 1855–1865, 1865–66, 1866–67, 1867–68, 1868–69, 1869–70, 1870–71, 1871–72, 1872–73 —*continued.*

Adler (J.). Nouveau Procédé d'Extraction du Jus de Betteraves. 8vo. Bruxelles, 1869

Agricolae (Georgii) De Re Metallica, Libri XII. Ejusdem, de Animantibus Subterraneis Liber, cum Indicibus diversis. Folio. Basileæ Helvet., 1621.

Aikin (A. and C. B.). A Dictionary of Chemistry and Mineralogy, with an account of the processes in many of the most important Chemical Manufactures; to which are added a description of Chemical Apparatus, and various useful Tables of Weights and Measures, Chemical Instruments, &c. Illustrated with fifteen Engravings. 2 Vols. 4to. London, 1807.

Akademie (kaiserliche) der Wissenschaften in Wien:

——— Almanach. 1855, 1856, 1858, 1859. 8vo.

——— Denkschriften. (Mathematisch-naturwissenschaftliche Classe.) 4to. Wien.

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2—1851.
3, 4—1852.
5—1853.
6, 7, 8—1854.
9, 10—1855.
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12, 13 wanting.
14—1858.
15, 16 wanting.
17—1859.
18—1860.
Band 19—1861.
20—1862.
21—1863.
22, 23—1864.
24—1865.
25—1866.
26—1867.
27—1868.
28—1869.
29—1870.
30—1871.

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——— Tafeln zu den Denkschriften (1850). 4to.

——— Die feierlichen Sitzungen. 29. Mai 1852, 1859, 1861. 8vo.

——— Festrede bei der feierlichen Uebernahme des ehemaligen Universitäts-Gebäudes durch die k. Akad. der Wissenschaften, gehalten am 29. October 1857, von Dr. Theodor Georg von Kurajan. 4to. Wien.

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Bände 4, 5—1850.
6, 7—1851.
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10, 11—1853.
12, 13, 14—1854.
15, 16, 17, 18—1855.
19, 20, 21—1856.
22, 23—wanting.
24 (Heft 3, Mai), 1857.
25 (Heft 1, Juni), 1857.
26—1857.
27 (Heft 1, Nov.), 1857.
28—1858.
Bände 29—1858.
30 (Nos. 13, 14)—1858.
31 to 34 wanting.
35 (Nos. 10, 11, 12).
36, 37, 38,—1859.
39, 40, 41, 42—1860.
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45, 46—1862.
47, 48—1863.
49, 50—1864.
51, 52—1865.
53, 54—1866.
55, 56—1867.

Continued.

Akademie (kaiserliche) der Wissenschaften in Wien—*continued.*

——— Sitzungsberichte. 1te u. 2te Classe.

Bände 57, 58—1868.
59, 60—1869.
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Bände 63, 64—1871.
65, 66—1872.
67, 68—1873.
Continued.

——— Register zu den Sitzungsberichten. Bände 1–10, 11–20, 21–30, 33–50, 51–60, 61–64.

Akademie (königlich-bayerische) der Wissenschaften in München.

——— Abhandlungen (Mathematisch-physikalische Classe). 4to.

Band 1—1829-30.
2—1831-36.
3—1837-43.
4—1844-46.
5—1847-49.
Band 6—1850–52.
7—1853-56.
8—1857-60.
9—1861-62.
10—1866.

——— Abhandlungen der naturwissenschaftlichen und technischen Commission derselben. Erster Band. 8vo. München, 1857.

——— Almanach, 1855–1859. 12mo.

——— Festreden, u. s. w. 4to.:—

——— —— Bauernfeind (Dr. C. M.). Die Bedeutung moderner Gradmessungen; 25. Juli 1866.

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—— Hermann (F. B. W.). Ueber den Anbau und Ertrag des Bodens im Königreiche Bayern. 28. März 1857.

——— ——— Ueber die Gliederung der Bevölkerung des Königreichs Bayern. (Festrede vorgetragen in der königlichen Akademie der Wissenschaften zu München, am 28. November 1855, zur Feier des Geburtsfestes Sr. Majestät des Königs.)

——— Kühn (Carl). Ueber das Klima von München (Festrede vorgetragen an der öffentlichen Sitzung der königlich-bayerischen Akademie der Wissenschaften zu München, zur Feier ihres fünf-und-neunzigsten Stiftungstages, am 28. März 1854); mit einem Anhange "den Gang der Witterungs-Elemente in der Umgebung von München," enthaltend.

Akademie (königlich-bayerische) der Wissenschaften in München: Festreden, u. s. w.—*continued:*

——— Lamont (Dr.). Denkrede auf die Akademiker Dr. Thaddäus Siber und Dr. George Simon Ohm. (Im Auszuge vorgetragen in der öffentlichen Sitzung der königl.-bayerischen Akademie der Wissenschaften zu München, zur Feier ihres sechs-und-neunzigsten Stiftungstages, am 28. März 1855.)

——— Liebig (Justus v.). Rede in der öffentlichen Sitzung der königl.-bayerischen Akademie der Wissenschaften zu München, am 28. März 1860.

——— ——— ——— am 28. Nov. 1861.

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Way (J. T.). Agricultural Pamphlets:—IV.

On the Composition and Money Value of the different Varieties of Guano. 8vo. London, 1859.

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——— Die Brunnenwasser der Stadt Karlsruhe. 8vo. Karlsruhe, 1866.—XI.

Wetherill (C. M.). On Adipocere and its Transformation. (Extracted from the Transactions of the American Philosophical Society, vol. xi., read January 19, 1855.)—XVI.

——— On Artificial Lactation. (From the Transactions of the Indiana State Medical Society. 1860.)—IX.

Wetherill (C. M.). Experiments with Ammonium-amalgam. (Silliman's Journal. Series 2, vol. xi. 1865.)—VII.

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——— On the Crystallization of Sulphur, and on the reaction between Sulphide of Hydrogen, Ammonia, and Alcohol. (Silliman's Journal. Second series, vol. xl. November, 1865.)—VII.

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——— On some of the products of the destructive distillation of Boghead Coal. Part 1. (Philosophical Transactions, 1857, Parts 1 and 2; 1858, Part 1.)—XIX.

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——— Address delivered at the Meeting of the British Association at Bradford. August, 1873. 8vo. XXII.

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——— On Isomeric Transmutation, and the views recently published concerning the compound nature of Carbon, Silicon, and Nitrogen. 8vo. Edinburgh, 1844.—VI.

——— On a simple Mode of constructing Skeleton Models to illustrate the Systems of Crystallography. (From the Transactions of the Royal Scottish Society of Arts, vol. iii, 1845.) 8vo.—I.

Wilson (George, M.D.). On the Composition of the Building Sandstones of Crailetli, Binnie, Gifnock, and Patrick Bridges. 8vo. Edinburgh, 1858.—VII.

——— On the Employment of Oxygen as a means of Resuscitation in Asphyxia, and otherwise as a Remedial Agent. 8vo. Edinburgh, 1845.—XII.

——— On Wollaston's Argument from the Limitation of the Atmosphere, as to the Finite Divisibility of Matter. (Trans. Roy. Soc., Edinb., vol. xvi, Part 1, 1845.)

Wilson (George, M.D.) and John Crombie Brown. Account of a Repetition of several of Dr. Samuel Brown's Processes for the Conversion of Carbon into Silicon. (From the Transactions of the Royal Society of Edinburgh, vol. xv, 1844.)—XVII.

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——— Bibliographische Notizen über die Zürcherischen Naturforscher, Geographer, Aerzte und Mathematiker, nebst Aufzählung der im Kanton Zürich vorhanden naturwissenschaftlichen Sammlungen. 4to. Zürich, 1846.—XVI.

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ABSTRACTS OF THE PROCEEDINGS

OF

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JANUARY—DECEMBER, 1886.

EDITED BY THE SECRETARIES.

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1886.

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ST. MARTIN'S LANE.

DATES OF ISSUE OF THE MONTHLY NUMBERS OF THE JOURNAL OF THE CHEMICAL SOCIETY TO FELLOWS.

January	number was issued	5th January.
February	„	2nd February.
March	„	3rd March.
April	„	2nd April.
May	„	3rd May.
June	„	31st „
July	„	1st July.
August	„	31st „
September	„	31st August.
October	„	9th October.
November	„	30th „
December	„	1st December.
Index	„ will be issued about	5th January.

LIST OF GRANTS MADE FROM THE RESEARCH FUND DURING THE YEAR.

£25 to Professor E. H. Rennie: for the investigation of the sweet principle of *Smilax glycyphylla*.

£10 to Mr. A. R. Ling: for the study of the action of halogens on halogen nitro-derivatives of phenols.

£20 to Mr. Gibson Dyson: for the further study of dicoumarine.

£5 to Dr. J. M. H. Munro: for the separation and study of the fluorescent substance in the testa of spurrey seed.

£10 to Mr. A. G. Perkin: for the study of the Indian colouring matter "Kamila."

£75 to Dr. W. H. Perkin, Junr.: for researches on the synthetical formation of closed carbon-chains.

£25 to Mr. R. Warington: for the purchase of a microscope for the study of the micro-organisms in soil.

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Name.	Proposed.	Elected.
Allan, James H.	February 4th	March 4th.
Akitt, Thomas	May 20th	June 17th.
Audley, James A.	November 4th	December 2nd.
Ball, E. J.	April 15th	May 20th.
Bamber, H. K. G.	December 17th, 1885.	March 4th.
Bell, Chichester A.	November 4th	December 2nd.
Bennert, Carl	March 4th	April 15th.
Bevan, J. W.	November 4th	December 2nd.
Blake, James, M.D.	May 6th	June 17th.
Blackett, Cuthbert R.	November 4th	December 2nd.
Bottomley, W. B.	,, ,,	,, ,,
Brothers, Horace Edward	November 18th	December 16th.
Burnett, W. E.	March 4th	April 15th.
Burton, Cosmo Innes	March 18th	,, ,,
Chaston, Alfred	May 20th	June 17th.
Chapman, Alfred C. H.	,, ,,	,, ,,
Clayden, Arthur William	March 18th	April 15th.
Coutts, Francis J. H.	November 18th	December 16th.
Cox, Ebenezer J.	November 4th	December 2nd.
Crompton, Holland	April 1st	May 20th.
Datta, P. N.	April 15th	May 20th.
Davenport, Bennet F.	June 3rd	November 18th.
Dawson, William Edward	April 15th	May 20th.
Day, Preo Loll	February 4th	March 4th.
Deane, Leopold M.	,, ,,	,, ,,
Diogo, August C.	May 20th	June 17th.
Dodd, W. Ralph	June 3rd	November 18th.
Doran, Robert D.	April 15th	May 20th.
Dormer, Richard	,, ,,	,, ,,
Dressel, Adolph	December 17th, 1885.	March 4th.
Ebworthy, H. S.	December 17th, 1885.	March 4th.
Ellis, John W.	December 3rd	,, ,,
Ferrey, Caleb	January 21st	March 4th.
Formoy, J. A.	February 4th	,, ,,
Fuller, John	November 4th	December 2nd.
Galt, Alexander	November 4th	December 2nd.
Garvin, Thomas F.	,, ,,	,, ,,
Glenfield, Francis W.	January 21st	March 4th.
Haga, Tamemasa	November 18th	December 16th.
Halliburton, William D.	April 15th	May 20th.
Hardy, Henry John	November 4th	December 16th.
Harris, Sydney J.	,, ,,	December 2nd.
Hart, Bertram H.	December 17th, 1885.	March 4th.
Henderson, Andrew	,, 3rd ,,	,, ,,
Hislop, Laurence	June 17th	November 18th.

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Hodgson, Christopher	March 18th	April 15th.
Holloway, George T.	December 17th, 1885.	March 4th.
Holt, George Crompton	November 4th	December 2nd.
Hoskins, A. P.	January 21st	March 4th.
Howson, G. W. S.	April 1st	May 20th.
Kawakita, Michitada	November 18th	December 16th.
Jones, A. Wentworth	April 1st	May 20th.
Johnson, John T.	„ 15th	„ „
Jowitt, Charles A. R.	May 6th	June 17th.
Kilpatrick, Charles	February 18th	April 15th.
King, John W.	March 18th	„ „
Kirby, H. E.	November 4th	December 2nd.
Kohn, Charles A.	„ „	„ „
Lang, William	December 3rd, 1885	March 4th.
Laurie, Arthur P.	„ „	„ „
Leach, Walter	November 4th	December 16th.
Leon, John T.	May 20th	June 17th.
Leissner, Henry A. B.	November 4th	December 2nd.
Ling, Arthur R.	March 4th	April 15th.
Lyons, Albert Brown	June 3rd	November 18th.
Macan, H. O'Donaghue	November 4th	December 2nd.
Mackay, James B. L.	„ „	„ „
Mackintosh, J. B.	„ „	„ „
McEwan, Peter	December 3rd, 1885.	March 4th.
Marks, Edward L.	November 4th	December 2nd.
Minty, Henry Oliver	March 18th	April 15th.
Morel, Frank	March 4th	„ „
Moos, M. N. A. F.	November 4th	December 2nd.
Newton, Walter	December 3rd, 1885	March 4th.
Obach, Eugene	December 17th, 1885.	March 4th.
Pendlebury, William H.	April 1st	May 20th.
Pentecost, Stephen James	November 18th	December 16th.
Phillips, Henry Joshua	„ „	„ „
Pilkington, Herbert	November 4th	December 2nd.
Pyke, L. S. M.	„ „	„ „
Quayle, Edwin	November 4th	December 2nd.
Quibell, Oliver	December 17th, 1885.	March 4th.
Ray, William	May 20th	June 17th.
Readman, James B.	June 3rd	November 18th.
Rée, Alfred	„ 17th	„ „
Remington, Joseph P.	May 20th	June 17th.
Richards, V. H.	June 17th	November 18th.
Richards, William	May 20th	June 17th.
Rickard, Forbes	„ 6th	„ „
Roose, Robson	March 4th	April 15th.
Ross, J. Galbraith	January 21st	March 4th.

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Saunders, William	May 20th	June 17th.
Schleselman, James	November 4th	December 2nd.
Sheshadri, P. Yeshwant	November 18th	December 16th.
Shimidzu, Tetsukichi	,, ,,	,, ,,
Shutt, Frank T.	June 17th	November 18th.
Silvester, Harry	November 4th	December 2nd.
Simpson, William S.	April 15th	May 20th.
Smith, Charles A.	May 20th	June 17th.
Smith, Edgar F.	June 3rd	November 18th.
Spencer, Richard	December 17th, 1885.	March 4th.
Stapleton, Joseph	November 4th	December 16th.
Starey, A. J.	January 21st	,, ,,
Sutton, F. Napier	December 3rd, 1885.	,, ,,
Thompson, C. M.	December 3rd, 1885.	March 4th.
Thompson, William Phillips	November 18th	December 16th.
Turner, Arthur	November 4th	December 2nd.
Twining, A. H.	,, ,,	,, ,,
Walker, Henry H.	April 15th	May 20th.
Walker, William	November 4th	December 2nd.
Whiteley, Richard Lloyd	March 18th	April 15th.
Wertheimer, Julius	December 3rd, 1885.	March 4th.
Williams, Reginald	November 4th	December 2nd.
Williamson, Sidney	January 21st	March 4th.
Wilmore, Edward	February 4th	,, ,,
Wright, W. T.	January 21st	,, ,,
Yoshida, Hikorokuro	November 18th	December 16th.
Young, Brougham	January 21st	March 4th.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 16. Session 1885-86.

January 21st, 1886. Dr. Hugo Müller, F.R.S., President, in the Chair.

Messrs. Charles Langert, W. J. Cousins, W. Watson Will, and G. H. Bailey were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Caleb Ferrey, M.B., C.M., B.Sc., Mainhead, Bondi, Sydney, N.S.W.; Francis W. Leeds, Glenfield, 69, Highbury New Park, N.; Arthur Percy Hoskins, 58, Wakehurst Road, New Wandsworth, S.W.; James Galbraith Ross, 14, Argyle Place, Grange, Edinburgh; Arthur John Starey, 8, Duncombe Road, Hornsey Rise, N.; Sidney Williamson, Fairholme, Esher, Surrey; William T. Wright, 15, Victoria Road, Bromhall Park, Sheffield; Brougham Young, Home Lyn, Woodberry Down, London.

The following papers were read:

1. "The Influence of Silicon on the Properties of Cast Iron." Part III. By Thomas Turner.

The paper is a continuation of those recently published by the author on the same subject (Trans., **47**, 577, 902). It is shown that the previous results strongly support the author's conclusions, although opposite opinions have been generally held.

The Woolwich Report, "Cast Iron Experiments, 1858," is considered in detail. This report included the chemical analyses and mechanical tests of 70 specimens of British cast iron. The author classifies these irons according to the amount of phosphorus present, and in different tables considers every specimen mentioned in the report. Some of the more important results are as follows:—

1. Only eight specimens were mentioned as being "too hard to turn;" seven of these contained under 0·9 per cent. of silicon, while the eighth was rich in phosphorus and sulphur. These facts strongly support the author's conclusion that a softening effect is produced by a suitable proportion of silicon.

2. The six best specimens mentioned in the report contained on an average 1·393 per cent. of silicon, while the author, from his own experiments, recommended about 1·4 per cent. The six specimens lowest in silicon are of intermediate quality, while the six specimens highest in silicon are of inferior quality. These results support the author's view that a suitable proportion of silicon is beneficial.

3. When the specimens are classified according to their proportion of phosphorus and arranged in tables in order of silicon present, a gradual improvement is noticed as the silicon increases until a certain point is reached beyond which point the metal deteriorates in quality. In one table, however (0·2—0·4 per cent. of phosphorus), no such regularity is observed; this is due to the small variations in silicon and the large alterations in the proportion of other elements present.

4. That the maximum points are as follows:—

With under 0·2 per cent. phosphorus	1·88	p. c. Si.
Between 0·4 and 0·6 per cent. phosphorus.	1·21	,,
,, 0·6 ,, 1·0 ,, ,, .	1·41	,,
Over 1 per cent. phosphorus	1·57	,,
English irons in the Appendix	1·03	,,
Foreign irons in the Appendix	1·33	,,
Mean	1·405	,,

The author also refers in detail to Sir William Fairbairn's experiments of 1853 on the influence of remelting on the mechanical properties of cast iron. It is shown that the results obtained may be entirely explained by the chemical changes which took place; and that when regarded in this light they illustrate the influence of silicon on cast iron very much in the same way as did the results previously published by the author.

Discussion.

Prof. Unwin said that Mr. Turner had done a service in removing the popular prejudice that silicon is a very injurious constituent of cast iron. This prejudice arose a long time ago, apparently from the difficulty experienced in smelting very rich iron ores containing much silica. Thus the Turkish Government in 1844 wished to utilise an exceedingly rich ore (magnetic ore containing 12 per cent. silica) found at Samakoff, but could not smelt it, and the difficulty was attributed

to the silica. Again about 1853 attempts were made to improve cast-iron guns, and Mr. Cochrane advised the use of Nova Scotia iron. This was tried at Woolwich, but the Chemical Department there refused to sanction its use on the ground that it contained too much silicon, notwithstanding that Mr. Fairbairn's mechanical tests were in its favour.

Prof. Unwin exhibited specimens of some of the bars produced in Mr. Fairbairn's 1853 experiments in the remelting of iron, and he stated that the iron was remelted in a brass furnace, not a cupola. From the analyses quoted of the bars tested in these experiments it appeared that the only chemical change which occurred in remelting was the change in the amount of silicon, which therefore seemed to be the sole cause of the variation in strength. But this was a fallacy: the methods of determining carbon in those days were faulty, and no distinction was drawn between graphitic and combined carbon. The change in properties on remelting was always attributed chiefly to the change from graphitic to combined carbon. Mr. Turner stated that he had found exceptional values of the modulus of elasticity. Now the determination of the modulus of elasticity was so difficult that hardly any measurement is to be trusted unless the measurements are made on suitable bars under suitable conditions; frequently the bars used are far too short. He was not prepared to agree that because a certain proportion of silicon was present, therefore the iron was good; and it was essential to bear in mind that in cast iron we want not strength so much as certain working qualities; mere crushing strength was of very little importance.

As supporting Mr. Turner's views, Mr. Pochin quoted an instance of an iron containing some amount of silicon being accepted by a manufacturer of very small castings as suitable in place of one with less which had been complained of as unsuitable on the ground that it contained too much silicon. He suggested that some of the discrepancies in analyses referred to by the author might really be due to difference in composition; different parts of one and the same pig or steel ingot often differ very much in composition. He had recently had occasion to notice great differences in quality in the two ends of steel sleepers, the one withstanding all tests, the other breaking readily.

Mr. Turner in reply said that he did not contend that a large proportion of silicon was good, but that when present in suitable proportion it improved the quality of the iron. No doubt the conversion of graphitic into combined carbon was a most important change, but the extent to which this took place probably in some way depended on the amount of silicon present; he had shown in a previous paper that grey cast iron can be made from white by addition of silicon.

He did not think that the serious discrepancies which he had called attention to could be explained in the manner suggested by Mr. Pochin.

2. "The Chemical Action of Pure Cultivations of *Bacterium aceti*." By Adrian J. Brown.

After referring to the work of Pasteur and others on acetic fermentation, the author describes his method of working and the means used for obtaining pure cultivations of *Bacterium aceti*. He then treats of the mode of growth and morphology of the organism. The different cell-forms observed agree with the drawings of *B. aceti* by Hansen and Zopf. The ferment is strictly ærobic.

After showing that *B. aceti* oxidises ethylic alcohol to acetic acid and that the acetic acid so formed is subsequently destroyed by the ferment, its action on other alcohols of the same series is studied. Normal propylic alcohol is freely oxidised to propionic acid, but methylic alcohol is not acted upon. Isoprimary butylic alcohol and amylic alcohol are also not attacked.

The action of *B. aceti* on certain carbohydrates is then described. Dextrose is freely acted on by the ferment; no alcohol or volatile acid is formed during the fermentation, the sole product being gluconic acid, the relation of which to dextrose is exhibited in the formulæ:—

Dextrose, $CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH).CH(OH)\cdot COH$,

Gluconic acid .. $CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot COOH$.

Cane-sugar is unaffected by *B. aceti*, even when the organism is made to grow freely in a solution containing it. This is true also of milk-sugar and starch.

Mannitol is shown to be completely acted upon by *B. aceti*, the main product being lævulose. A small proportion of a body possessing a cupric reducing power, but no action on polarised light, is also simultaneously formed. No acid is formed, the lævulose produced not being further acted on by *B. aceti*. Lævulose prepared from inulin is also not oxidised by the ferment, thus indicating a marked difference in the constitution of dextrose and lævulose. Using Kiliani's formula for lævulose, its relation to mannitol is shown by the formulæ:—

Mannitol, $CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH_2(OH)$

Lævulose, $CH_2(OH)\cdot CH(OH)\cdot CO\cdot CH(OH)\cdot CH(OH)\cdot CH_2(OH)$

As mannitol may be formed from dextrose by the action of sodium

amalgam, the oxidation of mannitol by *B. aceti* appears to afford a means of converting dextrose into lævulose.

Discussion.

The President remarked that the study of the effects produced by various organisms presents an enormous field for research; the results obtained by Fitz had already shown this. The experiments were also of interest as bearing on the examination of antiseptics, and pointed to the importance of ascertaining their effect upon a variety of organisms, as a given antiseptic might affect one kind and not another.

Dr. Armstrong said that Mr. Brown's results appeared to him to throw some light on the remarkable transformations undergone by the carbohydrates in plants and animals. It is well known that in some cases starch wanders from the leaves where it has been formed and is elsewhere again deposited as starch, as in the potato, for example; that in the sugar-beet it becomes cane-sugar, and in the dahlia and artichoke inulin; and that sometimes in animals it becomes milk-sugar. No clue has hitherto been obtained to these and similar changes. The conversion of mannitol into lævulose, however, indicates a possible mode of obtaining cane-sugar from starch, as it is unquestionable that a change such as that of starch into dextrose and then into mannitol takes place within the plant, and that individual cells may act upon the mannitol in the same way as *B. aceti* does, forming lævulose, which might then enter into reaction with dextrose. As regards the difference in behaviour of various carbohydrates, he thought that caution must be observed in reasoning from the formulæ ordinarily employed; probably even the simplest carbohydrates exist in solution as complex aggregates of several C_6 groups, and their behaviour much depends on the composition of these aggregates. Mr. Brown's observations were also of value as throwing light on the phenomena of fermentation. He (Dr. Armstrong) had long thought that fermentation took place in consequence of a something contained within the ferment-organism attaching itself to the molecule of the fermented substance; action thereupon set in at this point of attachment, and hydrolysis taking place the molecule was ultimately broken up: the function of ferments was, in fact, to localise the action, whether of water alone, or of water and atmospheric oxygen. Mr. Brown's observations on mannitol clearly proved that the organism exercised a selective influence.

3. "A Method of Separating and Estimating Zirconium." By G. H. Bailey, D.Sc., Ph.D.

When a solution of zirconia in dilute sulphuric acid is treated with excess of hydrogen peroxide, a white bulky precipitate is obtained consisting of an oxide of zirconium of the formula Zr_2O_5. This oxide seems to be possessed of very well-defined characters, and moreover the precipitation is a complete one. It is suggested that the reaction may be utilised as a means of obtaining pure compounds of zirconium, of separating zirconium—especially where it occurs in small quantities in minerals, and in quantitatively determining this element.

4. "Notes on an Analysis of Koppite." By G. H. Bailey, D.Sc., Ph.D.

The following are the author's results :—

		Knop and Rammelsberg.
Nb_2O_5	61·4	62·18
TiO_2	0·72	—
ThO_2	—	3·0
ZrO_2	3·39	—
Ce, La, Di oxides	6·89	6·69
FeO	3·01	1·80
CaO	16·61	16·00
MgO	1·62	0·4
Na	3·58	5·58
K	0·36	4·23
F.....	Not estimated	6·23

Discussion.

The President enquired how the titanium had been separated from niobium; he was not aware that any method had yet been devised. The discovery of titanium in the mineral was in itself an interesting fact; had the author taken the precaution of excluding Dysanalyte?

Dr. Bailey, in reply, said that the titanium was estimated in presence of the niobium by a colorimetric method, by means of hydrogen peroxide; the crystals were very carefully selected, and only the octahedral ones were analysed.

5. "The Monobromophthalic Acids." By G. Stallard.

Guareschi and Meldola have both assumed that the bromophthalic acid melting at 175° is the 1 : 2 : 4 modification, attributing the alternative formula COOH : COOH : Br = 1 : 2 : 3 to the acid melting at 139°. Guareschi obtained the acid of higher melting point by

oxidising the bromonitronaphthalene produced on brominating nitronaphthalene. The author, however, finds that α-bromonaphthalene is produced on eliminating the NO_2-group from Guareschi's bromonitronaphthalene; and that it yields γ-dibromonaphthalene (melting at 130°) on displacing the NO_2-group by Br. Hence he infers that the bromophthalic acid melting at 175° is the 1 : 2 : 3 modification; and he points out that this view is favoured by the fact that, according to Krüger, the melting point of the anhydride of the 1 : 2 : 3 chlorophthalic acid is much higher than that of the 1 : 2 : 4 modification. This conclusion, however, does not harmonise with Meldola's view of the constitution of the dibromonaphthylamine which he obtained from bromo-β-naphthylamine from Liebermann's bromonitronaphthalene.

6. "Benzoylacetic Acid and some of its Derivatives." Part IV. By W. H. Perkin, Jun., Ph.D., and A. Calman, Ph.D.

In the hope that methylic benzoylacetate might prove to be a crystalline substance, the authors have prepared it from methylic phenylpropiolate and sulphuric acid; but they could not obtain it otherwise than as an oil, and several of its derivatives were also found to be oils.

Ethylic methylbenzoylacetate is described. PCl_5 converts it into ethylic α-methyl-β-chlorocinnamate, $C_6H_5{\cdot}CCl : CMe{\cdot}COOEt$. By the action of sodium amalgam on its alcoholic solution, α-methyl-β-hydroxyphenylpropionic acid is produced. Ethylic propylbenzoylacetate is next considered, and its conversion into butylphenylketone by the action of dilute alcoholic potash is described; it yields ethylic α-propyl-β-chlorocinnamate on treatment with PCl_5. An account of ethylic isopropylbenzoylacetate and isobutylbenzoylacetate and of the corresponding ketones is then given.

The authors have further studied ethylic furfurandicarboxylate obtained by heating ethylic dibenzoylsuccinate with sulphuric acid.

7. "Mercury Sulphites and the Constitution of Sulphites." By Edward Divers, M.D., F.R.S., and Tetsukichi Shimidzu, M.E.

In formation, composition and reaction the mercury sulphites, according to the authors, are not ordinary salts, and supply many facts serving for the determination of the constitution of non-saturated oxygenous salts. The mercuric radicle, Hg, takes up and preserves a non-oxylic relation to sulphuryl with an energy comparable to that it exerts in its cyanide and iodide; this is the central conception in the chemistry of the mercury sulphites, and they are of opinion that without it all the peculiarities of these salts stand unexplained.

The paper is of great length; the salts which are described and discussed, and the formulæ attributed to them, are as follows :—

Mercuric sodium sulphite	$Hg<^{SO_2\cdot ONa}_{SO_2\cdot ONa}\cdot OH_2$
Mercuric hydrogen sulphite (known only in solution)	$Hg<^{SO_2\cdot OH}_{SO_2\cdot OH}$
Mercuric oxysulphite.....	$Hg<^{SO_2\cdot OHgO}_{SO_2\cdot OHgO}>Hg\cdot OH_2$
Mercuric mercurous or mercurosic sulphite	$Hg<^{SO_2\cdot O}_{SO_2\cdot O}>Hg_2\cdot 4OH_2$
Mercuric hypomercurous or hypomercurosic sulphite	$Hg<^{SO_2\cdot O}_{SO_2\cdot O}>Hg_3\cdot OH_2$

Only the first and third of these have been previously described. Normal mercuric and mercurous sulphites do not appear to be capable of existing.

Among the conclusions arrived at are the following :—In reduction by sulphurous acid, the acid is not as such or directly oxidised by the metallic salts reduced, but a sulphite is formed through changes in which reduction afterwards follows. Either, as in the case of mercurosic sulphite, a further quantity of the sulphurous acid or alkali sulphite resolves the salt into a double salt of part of the metal: the free metal, *e.g.*, mercurosic sulphite becomes mercuric hydrogen sulphite and mercury; or the sulphite suffers hydrolysis into metal and sulphuric acid.

Mercury and silver sulphites resemble organic sulphites (sulphonates) in undergoing hydrolysis into sulphuric acid and basic radicle, and in not oxidising in the air. The contrast they afford in this respect to most other metallic sulphites is good evidence of sulphites having a hemi-haloid constitution. Hydrolysis may in fact serve as a test of the constitution of an oxygenous salt: if the salt suffer hydrolysis into acid and metal, the salt is partly haloid; while if it yield acid and basic oxide it is wholly oxylic.

Sulphites are like haloid salts and unlike oxylic salts in the property which some of them display of parting with some of their chlorous radicle. Mercuric sulphite becomes mercurosic sulphite, much as manganic chloride becomes manganous chloride and cupric iodide or cyanide becomes cuprous; mercury and silver sulphites become metal and acid radicle, much as gold chlorides become gold and chlorine. There is a difference in the cases, but this is accounted for by the sulphites being hemi-oxylic salts—therefore requiring water to effect their decomposition. Sulphites are also like haloid salts in the considerable insolubility of their silver and mercury compounds in nitric acid; and they resemble iodides and cyanides

inasmuch as the double mercury and silver salts are stable and not decomposed by free alkalis.

8. "Potassium Chlorate." By Frank L. Teed, D.Sc.

The author in a previous paper arrived at the conclusion that the decomposition of potassium chlorate by heat may be represented by the equation $10KClO_3 = 6KClO_4 + 4KCl + 3O_2$. He has continued his experiments and finds that when the salt is very gently heated the decomposition more nearly approximates to that indicated by the equation $22KClO_3 = 14KClO_4 + 8KCl + 5O_2$, the majority of his results falling within the limits calculated from these two equations.

As bearing on the subject, the decomposition of potassium perchlorate by heat was investigated; it appears that in the earlier stages potassium chlorate is formed, but this disappears again long before the complete decomposition of the perchlorate is effected.

He finds that when the perchlorate is heated with manganese binoxide, it decomposes apparently without any chlorate being formed.

Some numbers obtained by Baudrimont, which had an apparent similarity to his own, are criticised, and it is pointed out that Baudrimont's methods of analysis must have been untrustworthy.

The author intends continuing his experiments.

Discussion.

Dr. Percy Frankland said that experiments made in the South Kensington Laboratory had given results in accordance with the equation $8KClO_3 = 2O_2 + 5KClO_4 + 3KCl$. Care had been taken to prevent mechanical loss by placing a glass wool plug above the chlorate; the decomposition had been effected at a known constant temperature; and the amount of residual chlorate had been determined.

Dr. Armstrong remarked that the results now brought forward made it more than ever probable that, as he had previously suggested, the perchlorate simultaneously underwent decomposition even at a temperature below that at which it decomposes when heated alone: a considerable amount of heat is developed in the decomposition of potassium chlorate, and it was therefore to be expected that the amount of perchlorate formed would be less, and the amount decomposed greater, and hence that more oxygen would be obtained, when the decomposition was effected more rapidly, as the temperature would be locally higher.

Dr. Teed said that the results quoted by Dr. Percy Frankland confirmed his statement that the ratio of oxygen to chloride depends on

the way in which the decomposition is effected; Dr. Frankland would find less oxygen produced at a lower temperature.

9. "On the Sugars of some Cereals and of Germinated Grain." By C. O'Sullivan, F.R.S.

My attention has been called to a paper by Kjeldahl, of the Carlesberg Laboratory, Copenhagen, published in the Transactions of that Institution, in which this subject is treated. The methods employed are pretty much the same as those described by me, and the results obtained are practically confirmed by my work. Priority of publications of the chief points belongs, therefore, to Kjeldahl.

I regret very much that I should have missed this work of Kjeldahl, and I take the earliest opportunity of putting the matter right as far as I can. I may, however, say, in justice to myself, that there is sufficient novelty in the mode of treatment and in the details of my work to justify the publication of it even though I had seen Kjeldahl's paper.

10. "Note on the Chemical Formula for Wool Keratine." By R. Lloyd Whiteley, Lecturer on Dyeing at University College, Nottingham.

Having occasion to calculate the approximate formula for the keratine found in wool fibre, according to "Bowman's Analyses" (p. 170, "Structure of the Wool Fibre," by F. H. Bowman) I was surprised to find what a different result I obtained from that given by Mills and Takamine (*Chem. Soc. Trans.*, 1883, **43**, 142), and quoted by Bowman. I therefore referred to Mills' data to ascertain wherein the difference lay, and found that in *Gmelin's Handbook*, **18**, 351, from which the numbers had been obtained, there was an evident misprint, the values of the hydrogen and nitrogen in the percentage numbers being interchanged. This was confirmed on reference to two of the original papers, viz., Märcker and Schulze (*Annalen*, **40**, 193—207), and Scherer (*Ann. Pharm.*, **40**, 53).

Instead, therefore, of the formula $C_{42}H_{157}N_5SO_{15}$, as given by Mills (*loc. cit.*), the corrected results yield the formula $C_{41}H_{71}N_{12}SO_{14}$, obtained from the mean figures C 49·96, H 7·11, N 16·65, O 3·39, S 22·89 (by difference), in which probably the nitrogen is too low, and the oxygen correspondingly high.

Taking Dr. Bowman's later analyses we obtain the approximate formula $C_{43}H_{71}N_{13}SO_{13}$, from the mean figures C 50·27, H 7·05, N 18·37, S 2·90, O 20·40.

These figures are not quite free from objection, the carbon being probably rather high; but considering the difficulty of completely

purifying the fibre from every trace of mechanically adhering mineral matter, it is probable that either of the two formulæ may be taken as closely resembling the true empirical one. This would apply to wool only, for, though the analysis of other keratines, such as those of hair, horn, &c., closely agree in the amount of carbon and hydrogen, and fairly well in the amount of nitrogen, in the case of sulphur and oxygen they are proportionably much more divergent, so that it is impossible to represent them by any one formula.

11. "Some Derivatives of Thiourea." By George McGowan, Ph.D., F.R.S.E.

In continuation of his examination of the derivatives of methyl-sulphonic acid (*J. pr. Chem.*, 1884, **30**, 280), the author has submitted thiourea to the action of trichloromethylsulphonic chloride. If the chloride, $CCl_3 \cdot SO_2Cl$, be added to a cold aqueous solution of thiourea, no reaction takes place until after long standing, but on applying heat the chloride gradually dissolves, sulphur being deposited. On adding the chloride to a cold or nearly cold solution of thiourea in 80 or 90 per cent. alcohol, much heat is developed, and a mass of needle-like crystals separate out, the quantity being much increased by the subsequent addition of ether. The product is identical with the *dithiourea dichloride*, $(CSN_2H_4)_2Cl_2$, obtained by Claus by acting on thiourea with chlorine (*Annalen*, **179**, 139). The same compound is obtained by the action on thiourea of mono- and di-chloromethyl-sulphonic chlorides and of phosphorus oxychloride, but the author failed to obtain it with acetyl chloride. When allowed to crystallise out from 90 per cent. alcohol on a microscopic slide, it forms highly characteristic, apparently monoclinic, plates. It cannot be recrystallised from water or alcohol as the solutions invariably deposit sulphur. An aqueous solution strongly acidified with chlorhydric acid may, however, even be heated with impunity. It is perfectly stable at ordinary temperatures.

If dilute nitric acid be added to a moderately concentrated aqueous solution of the dichloride, a crystalline precipitate is produced in the form of jagged daggers or long sword-like plates, consisting of the nitrate $(CSN_2H_4)_2(NO_3)_2$. These crystals were also observed to be formed in the mother-liquor from the preparation of thiourea nitrate, CSN_2H_4,HNO_3. The salt is almost insoluble in dilute nitric acid; more soluble, although sparingly, in water; practically insoluble in cold absolute alcohol and in ether. This is a comparatively stable compound, and in this respect differs from the thiourea nitrate described by Reynolds; but the author suggests that the instability of the latter may have been due to the presence of a small quantity

of free nitric acid. A solution of potassium nitrate also produces a precipitate of the above nitrate in a cold aqueous solution of dithiourea dichloride.

If iodine chloride or trichloride be added to a cold alcoholic solution of thiourea, dithiourea dichloride is formed, iodine separating. If potassium iodide and thiourea dichloride be suspended together in absolute alcohol, they react to form thiourea, potassium chloride and iodine. *Dithiourea diiodide*, $(CSN_2H_4)_2I_2$, can, however, be prepared by rubbing together in a mortar *pure* thiourea and iodine in the proportion of their molecular weights, sufficient alcohol being added to make a pasty mass; the reaction succeeds best when only small quantities are used. Once it is prepared, the diiodide is quite stable and can be preserved in a dry tube; it crystallises in long colourless prisms. It is at once decomposed by water, alcohol and ether, iodine separating, but not by benzene. On heating the aqueous solution, or on addition of caustic alkali, sulphur separates, this separation of sulphur being characteristic of the dithiourea salts. Addition of dilute chlorhydric acid does not cause the separation of iodine in the cold, but on heating the solution iodine is freely liberated, but no sulphur is precipitated: hence it is more easily decomposed under these conditions into iodine and thiourea than into sulphur, hydrogen iodide, thiourea and cyanamide (or derivatives thereof), these latter being the products which should result, according to Claus's observations on the dichloride.

The results are given of the complete analyses of the salts described in the paper.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Principles of Thermal Chemistry: by M. M. P. Muir, assisted by D. M. Wilson: London, 1885: from the Author.

Transactions of the Sanitary Institute of Great Britain: Vol. vi, 1884–5: London, 1885: from the Council.

Brewing with Raw Grain: by T. W. Lovibond: London, 1883: from the Author.

Chemistry; General, Medical, and Pharmaceutical: by J. Attfield: eleventh edition: London, 1885: from the Author.

Year Book of Photography for 1886: London: from the Editor.

Die Schwingungsknoten. Theorie der Chemischen Verbindungen:

von M. N. Teplow: aus dem Russischen übersetz: von L. Jawein: St. Petersburg, 1885. from the Author.

Lightning Conductors, their History, Nature, and Mode of Application: by R. Anderson: London and New York, 1885: from the Author.

Ausfuhrliches Lehrbuch der Chemie: von H. E. Roscoe und Schorlemmer: Zweite vermehrte Auflage: Band I: Nichtmetalle: Braunschwig, 1885: from the Authors.

II. *By Purchase.*

Thermochemische Untersuchungen: von J. Thomsen: Band IV: Organische Verbindungen: Leipzig, 1886.

Titles of Papers of interest to Chemists recently read before Societies in the United Kingdom:—

"On the Action of Sunlight on Micro-organisms, &c., with a Demonstration of the Influence of Diffused Light." By Dr. Arthur Downes.

Royal Society of London, January 14th.

"On the Foundations of the Kinetic Theory of Gases"—

(*a.*) "On the ultimate average Distribution of Energy among Systems of Colliding Spheres."

(*b.*) "On the Length of the Mean Path among Equal Spheres." By Professor Tait.

"On the Temperature of Loch Lomond." By J. Y. Buchanan, Esq.

"On Dew." By John Aitken, Esq.

"On the Salinity of the Water about the Mouth of the Spey." By Hugh Robert Mill, Esq., B.Sc., and T. Morton Ritchie, B.Sc.

"On the Distribution and Significance of Micro-organisms in Water." By A. Wynter Blyth, Esq.

"On Systems of Colliding Spheres." By Professor Tait.

"On the Effect of Pressure on the Maximum Density Point of Water." By the Same.

"On the Relation between the Densities and the Atomic Weights of the Elements." By Professor Crum Brown.

"On the Partition of Energy among Systems of Colliding Spheres." By Professor Tait.

"On an Improved Form of Water-Collector." By H. R. Mill, Esq., B.Sc., F.R.S.

"On a Repetition of Berthelot's Experiment on the Tenacity of Water and its Adhesion to Glass." By H. G. Creelmann, B.A.

Royal Society of Edinburgh, December 7th and 21st; January 4th and 18th.

"Some Thermodynamical Relations." By Professor Ramsay and Dr. Young.

"Note on the foregoing Paper." By Professors Ayrton and Perry.

Physical Society, November 28th, and January 23rd.

"On Gas Producers." By Mr. F. J. Rowan.

Institution of Civil Engineers, January 15th.

SALE OF THE "ABSTRACTS OF PROCEEDINGS."

The Council having resolved to place the "Abstracts of Proceedings" on sale at a price of *7s. 6d.* per annum, intending subscribers and Fellows who desire to purchase extra copies are requested to apply without delay to Mr. Van Voorst, Paternoster Row, London, E.C.

At the meeting on February 4th, Dr. Klein, F.R.S., will deliver a lecture on "Methods of bacteriological research from a biologist's point of view."

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 17. Session 1885-86.

February 4th, 1886. Dr. Hugo Müller, F.R.S., President, in the Chair.

Messrs. Robert G. Cristopher, George E. R. Ellis and E. E. H. Thorne were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. James Henry Allan, 6, St. Chrysostom Street, Liverpool; Leopold Mandeville Deane, 52, Elswick Road, Newcastle-on-Tyne; Preo Loll Day, 4, Bradon Street, Calcutta; James Arthur Formoy, 12, Railway Approach, London Bridge; Edward Willmore, 69, Lichfield Road, Bow, London, E.

The following note was read:

12. "The Chemical Formula for Wool Keratine." By Edmund J. Mills, D.Sc., F.R.S.

In the last number of these Proceedings, Mr. Whitely points out in Abstract No. 10 that Mills and Takamine gave (*Chem. Soc. Trans.*, 1883, 142) a necessarily wrong formula for wool, their calculation having been based on data in Gmelin's *Handbook*, **18**, 351, where H is misprinted for N. Mr. Whitely then deduces from the corrected results the formula $C_{41}H_{71}N_{12}SO_{14}$.

I wish to point out in the first place that, in the paper by myself and Takamine, the formula of wool was merely an incident, the main object being to give an account of the absorption of weak reagents by cotton, silk and wool. In the second place, I myself noticed the misprint in Gmelin's *Handbook* as long ago as last May (*Journ. Soc. Chem. Ind.*, 1885, 328) and calculated out for wool the corrected formula $C_{39}H_{65}N_{11}SO_{13}$, which agrees well with the results of its destructive distillation.

A lecture was delivered on—

13. "Methods of bacteriological research from a biologist's point of view." By Dr. Klein, F.R.S.

The object of the lecture was to bring before the Chemical Society the methods used at present by pathologists in the investigations of micro-organisms associated with disease. These methods, thanks to the investigations of Koch, are greatly in advance of those hitherto employed by chemists in the investigation of the activity of bacteria. The enormous amount of work that has been done by chemists since the memorable investigations of Pasteur on fermentation and putrefaction, if viewed in the light of the modern bacteriological methods, is in a great measure unsatisfactory and imperfect, more so than will be conceded by chemists. This unsatisfactory state is chiefly due to the imperfect methods employed. Specific chemical action is ascribed to certain organisms, because these were found present in the substances examined, no regard being paid as to whether these organisms were alone active or whether they were only concomitant and dependent on the activity of others.

Numbers of instances can be adduced to prove this: amongst them may be mentioned the assertions that alcoholic fermentation is produced by *Mucor racemosus*, and also by a bacillus besides saccharomyces; that the ammoniacal fermentation of urine is due to a bacillus; that the lactic acid fermentation is due to a micrococcus and also to a bacillus.

To determine whether a definite chemical process is produced by a definite organism, and which, it is necessary to prove—(1) that the substances to be acted upon are at the outset free of any accidental organisms; (2) that the particular organism to which the definite chemical activity is ascribed is the only one concerned in this process.

The methods used must fulfil these elementary conditions, that is to say:—(1) the materials used must be sterile at the outset, and protected from accidental contamination; (2) the specific organism must be obtained in pure cultivations, and this purified organism must be capable of producing the specific chemical change.

Viewed in this light few of the assertions hitherto made bear criticism. As one of the most striking instances, it may be mentioned, that notwithstanding the enormous amount of knowledge gained by chemical research into the changes of proteid bodies during putrefaction, there is no reliable answer yet given to the questions—Which organism or organisms are concerned in this complex process? Which part of the process is due to which organism? Is the analytical process by which proteids are carried down to relatively simple nitrogenous principles done by one or more organisms and by

which ? Is the production of the alkaloids known as ptomaines due to the same organism, or organisms which started the process of putrefaction ?

Another equally important series of investigations refers to the process of nitrification; here also no definite answer can be given. So also the chemical changes due to the growth of moulds are waiting for investigation.

When chemical research begins to adopt such methods as are employed by pathologists, but not till then, its results will be unequivocal.

The methods used for sterilising materials, for studying and recognising the morphological characters of organisms, for obtaining pure cultivations, and for inoculating nutritive materials with them were then minutely described.

Discussion.

Prof. Frankland, after dwelling on the importance of intercourse between biologists and chemists, said that he must plead guilty to the charge of having neglected precautions now known to be necessary when making his experiments on the fermentation of urine; he could, however, urge that there were extenuating circumstances, as the experiments were carried out 10 years ago when the necessity of such precautions being taken was not yet realised. He did not contend that the vibrios observed by him were the sole agents, but they were for days apparently almost exclusively present. It appeared to him that a point of primary importance brought forward by Dr. Klein was the fact that certain pathogenic organisms only develop at a relatively high temperature. It was probable that in the future the study of the chemical effects of organisms would be of greater service even than that of morphological characters as a means of differentiating various organisms. As regards *Mucor racemosus*, the statements in his paper were derived from the published researches of Dr. James Bell.

Mr. Warington described the conditions under which his experiments on nitrification were made. The solutions contained a very small proportion of nutritive matter, and the action was extremely slow: after three or four days a slight turbidity was observed, but nitrification did not set in until after about one month. He had made four or five successive cultivations, more being impossible by reason of the slowness of the action.

Dr. Percy Frankland said that, as Dr. Klein had properly stated, he had not asserted that the number of organisms found present on his plates was the number of organisms present in the water examined.

His experiments were made not so much with the object of discovering pathogenic organisms, but in order to study what took place in the ordinary processes of water purification. Of all known media, he thought that none was so universally applicable to the cultivation of micro-organisms as gelatin-peptone. The danger from air contamination was perhaps overrated. To illustrate how very slight is the contamination, he had recently exhibited a series of 12 plates put up with sterilised water, and of these only one had a growth upon it. He had recently made experiments with air confirming Hesse's observations, having found only 10 organisms in 20 litres—this, however, being in snowy weather. He had also made experiments on the number of organisms which fell upon a plate of gelatin such as was employed when working according to Koch's directions, and had found about two per minute. He thought that the experiments on fermentative action hitherto made were worthless from neglect of the precaution to employ pure cultivations.

Dr. Armstrong said that it undoubtedly was most important that the necessity of using pure cultivations should be impressed upon the chemist, but the work hitherto done in this field, far from being worthless as Dr. Percy Frankland had stated, was absolutely of almost as great value as if pure organisms had been dealt with. In most cases of putrefactive change the products were very numerous, their separation and identification was excessively difficult, and in not a few instances they were new to the chemist. Until the chemical methods of examining such products had been perfected, it was useless to incur the great labour involved in obtaining pure cultivations on a sufficient scale. This had been clearly recognised by most of the recent workers on the subject.

Mr. Ekin inquired if the organisms present in water might not play the part of useful scavengers. Evidence of this would, he believed, ere long be forthcoming.

Dr. Thudichum observed that the biologist working with impure ferments could be compared to the chemist employing impure reagents. The results of the life of microzymes were to a large extent chemical, as was known from ordinary fermentation; this was equally true of ferments which caused diseases. Thus in splenic fever, which he had investigated on a farm in Leicestershire, where it was endemic, he had found all hæmochrom transformed into methæmoglobin, and the spleen filled with crystals of albuminous decomposition products. In cholera a poison was formed by the bacilli which affected the muscles, and by fluidifying the colloids caused sinking of temperature, or the algid stage. In all diseases, however, the presence of bacilli, as in all fermentations, led to the evolution of heat, which with its attendant symptoms was termed fever. Fever heat had two sources, one was

increased combustion, another the liberation of latent or atomic heat, which was peculiar to the bioplasm. Now this liberation of atomic heat under the influence of the bacilli or their products led to a remarkable consequence, namely, a contraction of the atomic volume of the bioplasm; and when the tissues had attained the smallest atomic volume compatible with their function, bacilli could no longer live or thrive in them; the contracted bioplasm had attained to the state of immunity from the bacilli and their products. This state of immunity was attained through the action not only of specific bacilli, but also of their modification called vaccines. He agreed with Dr. Armstrong in two particulars concerning the chemical treatment of questions connected with bacilli. The fermentations might be studied with impure ferments, provided the processes were on a large scale, and a recognisable particular ferment prevailed. All possible decomposition products might be investigated first, and then the results of fermentations with pure ferments, or pure cultivations of bacilli would be much easier of discovery. In particular, as a pathologist, he was quite certain that investigations of a chemical kind on the changes effected by microzymes in the composition of animal tissues and fluids would not be adequately successful before the entire chemistry of these substances and all their decomposition products was completely known.

The President asked Dr. Klein whether the statement had been confirmed that *B. amylobacter* loses its specific character by cultivation in oxygenated media, and when its spores are heated.

Dr. Klein, in reply, said that he agreed with Prof. Frankland that the chemical aspect of the problem was the important one to study in the future; at present it was entirely unknown how the diseases associated with the presence of anthrax or the tubercle bacillus, for example, were produced. Light had in most cases a deleterious influence on the growth of bacteria; but some live only in light, and it had been stated that the so-called *Bacterium photometricum* lived only when exposed to a definite part of the spectrum. Dr. Percy Frankland had somewhat misunderstood him: he certainly thought that the gelatin method was the most useful one to employ in determining the number of bacteria in two given specimens of water. But he did not agree that gelatin-peptone was the most universally applicable medium; several organisms would grow in agar-agar, but not in gelatin, and blood serum was certainly better—indeed he did not know any organism which would not grow in it. As regards the struggle between organisms, there were cases known of non-pathogenic causing the destruction of pathogenic organisms present along with them. With reference to the employment of pure cultivations, what he had desired to point out was that the statements that certain

chemical changes were brought about by certain organisms were based upon insufficient evidence—he wanted to have them placed beyond question by the use of pure cultivations. Changes such as were referred to by the President certainly took place; thus Pasteur had found it possible to alter the functions of the *Bacillus anthracis*.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

On the Spectra of the Gases and Vapours evolved on heating Iron and other Metals, with Photographs and Map of Spectra: by J. Parry: Pontypool, 1885. from the Author.

II. *By Purchase.*

Lehrbuch der Anorganischen Chemie: von V. Richter: 5te neu bearbeitite Auflage: Bonn, 1886.

Mikroskopische Physiographie der Mineralien und Gesteine: von H. Rosenbusch: 2te gänzlich umgearbetite Auflage: Band I: die petrographisch wichtigen Mineralien: Stuttgart, 1885.

Lehrbuch der Agriculturchemie in vierzig Vorlesungen: von A. Mayer: 3te Auflage: Band I, erste Hälfte; Band II, erste Hälfte: Heidelberg, 1885.

At the next meeting on February 18th, there will be a Ballot for the Election of Fellows, and the following papers will be read:—

"On the Constitution of Undecylenic Acid, as indicated by its Magnetic Rotation; and on the Magnetic Rotation, &c., of Allylacetic Acids and Ethylic Diallylmalonate." By W. H. Perkin, F.R.S.

"On Reactions supposed to yield Nitrosyl Chloride." By W. Collingwood Williams, B.Sc.

"On the Condition in which Silicon exists in Cast Iron." By A. E. Jordan and T. Turner.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 18. Session 1885-86.

February 18th, 1886. Dr. Hugo Müller, F.R.S., President, in the Chair.

The certificate of Mr. Charles Kilpatrick, Dearnley, near Rochdale, Lancashire, was read for the first time.

The following changes in the Council, proposed by the Council, were announced:—

As Vice-Presidents: Prof. Dewar, F.R.S., and Mr. David Howard, vice Dr. Schunck, F.R.S., and Mr. W. Weldon, F.R.S. (deceased).

As Members of Council: Messrs. J. A. R. Newlands, S. U. Pickering, Prof. Ramsay and Dr. Stevenson, vice Dr. E. Atkinson, Prof. G. C. Foster, F.R.S., Mr. Ludwig Mond and Mr. C. O'Sullivan, F.R.S.

Prof. Wyndham Dunstan, Dr. Percy Frankland and Mr. Makins were appointed by the Meeting to audit the Society's accounts.

The following papers were read:—

14. "The Constitution of Undecylenic Acid as indicated by its Magnetic Rotation; and on the Magnetic Rotation, &c., of Mono- and Di-allylacetic Acids and Ethylic Diallylmalonate." By W. H. Perkin, Ph.D., F.R.S.

When investigating the magnetic rotation of compounds (Trans., 1884, 421) undecylenic acid was amongst those selected for examination as examples of the series of unsaturated monobasic acids having the formula $C_nH_{2n-1}\cdot COOH$. The numbers obtained, however, were lower than was expected, and did not appear to be consistent with those given by other members of this series, and were therefore kept

back for the purpose of further investigating the apparent discrepancy.

Both the acid and its ethylic salt were examined. The acid, purified by rapid distillation under reduced pressure (b. p. 230—235° at 130 mm.), gave a molecular rotation of 12·547. The ethylic salt boiled at 263·5—265·5° (corr.), and gave a molecular rotation 14·530.

Comparing these numbers with those of the corresponding saturated compounds, we get—

		Difference due to unsaturated character.
Undecylenic acid.....	12·547	+ 0·897
Undecylic ,, ...	11·650	
Ethylic undecylenate	14·530	+ 0·890
,, undecylate	13·640	

On reference to the table given in the author's former paper (Trans., 1884, 561), it will be seen that these differences are much lower than those (1·112) obtained for ethylic α-crotonate and oleate, but very nearly equal to those (0·914) found in the case of allyl substitution-products.

As these numbers were obtained before the author became aware of the influence of the magnetic field on the optical parts of the polarimeter, it was deemed advisable to re-examine the ethylic salt. The molecular rotation then obtained was 14·543, thus making the difference due to saturation 0·903, or almost identically that previously found with unsaturated compounds containing the allyl-group. As this appeared to indicate that undecylenic acid is an allyl compound, it was determined to examine allylacetic acid for the purpose of comparison. This was prepared by heating allylmalonic acid as long as carbonic anhydride was evolved and fractioning the residue. It boiled at 185—188° (corr.), and gave a molecular rotation of 6·426. From this we get almost the same difference as with the undecylenic compounds :—

Allylacetic acid.....	6·426
Valeric ,, ...	5·508
Difference	0·918

It is thus seen that undecylenic acid and its ethylic salt possess magnetic rotations which are peculiar to mono-allyl derivatives of the fatty acids.

The next question is as to the position of the allyl-group, as it is probable that the magnetic rotation would be the same whether it were, for example, an allyl-hexyl-acetic acid or an allyl-octylic acid: $C_3H_5{\cdot}CH(C_6H_{13}){\cdot}COOH$ or $C_3H_5{\cdot}C_7H_{14}{\cdot}COOH$. But Krafft has shown that when oxidised with nitric acid it yields normal

sebacic acid, and there can therefore be scarcely a doubt that undecylenic acid is allyloctylic acid, $CH_2{:}CH{\cdot}CH_2(CH_2)_7{\cdot}COOH$.

Whilst working on this subject it was thought interesting to prepare and examine diallylacetic acid. This was made from diallylmalonic acid, and boiled at 227—227·5° (corr.). It gave a molecular rotation of 10·344. The molecular rotation calculated for octylic acid is 8·577. There is thus a difference of 1·767 for the influence of the two allyl-groups. Deducting 0·903 for the first allyl-group, we get 0·864 for the second—a result consistent with previous results (see former paper), which showed that the influence decreases with successive displacements.

The redetermination of the molecular rotation of ethyl diallylmalonate in a freshly-prepared specimen gave 15·025, or a number differing by only 0·027 from that (14·998) given in the former paper.

15. "Reactions supposed to yield Nitroxyl or Nitryl Chloride." By W. Collingwood Williams, B.Sc.

Direct union of chlorine and nitrogen peroxide does not take place either at a red heat or at 150° C., nor does the action of chloranhydrides (such as phosphorus oxychloride or sulphuryl chloride) on nitric acid or nitrates yield nitryl chloride.

When chlorine and nitric peroxide are passed through a red-hot tube the product is a mixture of nitric peroxide and nitrosyl chloride containing chlorine in solution, while oxygen gas is liberated. This result is due to the dissociation of NO_2 into $NO + O_2$ at a red heat.

When the tube is heated to 150° C. only, no appreciable change occurs, the product being a solution of chlorine in the peroxide, and an exactly similar product is yielded by all the other methods examined.

16. "The Condition of Silicon in Cast Iron." By A. E. Jordan and Thomas Turner.

The authors have endeavoured to ascertain whether crystallised silicon can be separated from cast iron. They refer to the work of Wöhler, Richter, and others, who believed that they had obtained crystals of silicon, and also to the experiments of Snelus, Morton and Tilden, who were unable to separate silicon from cast iron in this form.

1. Several irons, including a specimen of pig containing 9·8 per cent. silicon, were submitted to magnetic examination. Though both graphite and slag could be separated by means of the magnet, it was not found possible to separate silicon in this manner.

2. The residue left after prolonged boiling with dilute hydrochloric acid was then studied. After drying, the graphite was burned off in a muffle, and the remainder examined for silicon. In no instance was silicon found; but in the case of a pig with 10·3 per cent. silicon, black scales were obtained of very difficultly decomposable iron silicide. These scales appear to closely resemble in properties the so-called graphitic silicon of some other observers. In the residue before roasting the authors found a quantity of substance resembling Wöhler's "leucone," the "silicon formanhydride" of Friedel and Ladenburg.

3. Lastly, graphitic matter from iron was examined. For the two specimens used they are indebted to Dr. Percy. The first was graphite from Dowlais, which had previously been examined by Dr. Percy, who suggested that it might contain crystallised silicon ("Iron and Steel," p. 145). It was found to be nearly pure carbon, and to be almost entirely free from silicon in any form. A specimen of kish, from Clarence Works, Middlesbro', was also examined, but in this case too no crystallised silicon was found.

The authors conclude that silicon is present in cast iron in the form of silicide, being probably a solidified solution in the excess of iron.

Discussion.

The President remarked that the results now brought forward pointed to the importance of direct synthetic experiments with silicon and iron as a means of ascertaining whether graphitic silicon can separate from iron under any conditions. Since it had been shown that the supposed crystalline modifications of boron were compounds with aluminium and carbon (Hampe, *Annalen*, 1876, **183**, 75), even the existence of a graphitic silicon appeared doubtful.

Mr. Turner said, that although he had not been able to make such experiments, he had examined irons containing up to 10 per cent. of silicon, and had always found the silicon to be present in the one form.

Sir Frederick Abel desired to express his concurrence in the conclusions arrived at by the authors, that there appeared to be no grounds for considering that silicon might exist in cast iron in the graphitic or crystalline form, or that this element might occur in two different conditions in cast iron, as carbon did. The results of very numerous experiments and the careful examination of many graphitic residues obtained from cast iron, had long since led him to these conclusions, but he hesitated referring to his own special experience of many years back in connection with the chemistry of cast iron, after the remarks which Professor Unwin was reported to have made on the occasion of Mr. Turner's last paper as to the condition of the

chemist's knowledge of cast iron 30 odd years ago. He had been as much surprised as amused to learn that at about the date when certain questions relating to a supply of iron to Woolwich arose, to which Professor Unwin had referred, the methods of determining carbon were faulty, and no distinction was drawn between graphitic and combined carbon. It was true that the analytical results given in the Woolwich Report, "Cast Iron Experiments, 1858," included statements of the proportions of graphite only in the partial analyses of samples then carried out for a special object; but in an Official Report, published two years previously by the War Office, the results of analyses of a number of specimens of cast iron used in the manufacture of ordnance included the items of "total carbon" and "carbon as graphite." In a paper contained in the Quarterly Journal of this Society for 1857, the proportions of *combined carbon* and of graphite existing in specimens of cast iron of foreign manufacture were also given by Sir Frederick. As regards the methods of analysis practised in those days, and which had been for some time previously taught at the School of Mines and elsewhere, they were in all essential respects similar to and as trustworthy as those now in use. He had learned with surprise that the eminent engineer who had made those criticisms on the work of 30 years ago, had thought it sufficient for his purpose to refer only to the work of one who certainly was never accepted by chemists an an authority on iron analysis.

As regards the matter of the Nova Scotia iron to which Professor Unwin had referred, and which was dealt with in 1858, not 1853, it was right he should state that a quantity of iron called Nova Scotian, supplied for gun-manufacture, was rejected, *not* "because the Chemical Department refused to sanction its use on the ground that it contained too much silicon," but because, instead of being a grey iron somewhat siliceous but otherwise of high quality, having the characters of charcoal-iron—as was the case with the sample of Nova Scotia iron which led to the purchase of a supply, it consisted in large proportion of white and light mottled iron, some of which contained as much as from 1 to 2 per cent. of phosphorus. Certain experiments were made on the effect of melting selected samples of this supply high in silicon, with the result that the strength of the metal was increased without a very material alteration in the proportion of silicon; but these results had no bearing upon the fitness of even this metal to resist powder-strains, nor upon the question whether the supply should not be rejected. The matter having been submitted to arbitration, Mr. Fairbairn, as umpire, decreed in favour of the rejection. In conclusion he ventured to assure Professor Unwin that, by reference to the literature of that time, he would find

that chemists were by no means far behind their brethren of the present day in regard to their knowledge of methods of analysis and properties of cast iron.

17. "Certain Aromatic Cyanates and Carbamates." By H. Lloyd Snape, B.Sc.

The author finds that on heating phenyl cyanate with pyridine it is converted into *diphenyl dicyanate*, $C_{14}H_{10}N_2O_2$. He has prepared a number of dicyanates by the action of carbonyl chloride on diamines, and has studied their behaviour with alcohols, as in his previous work on phenyl cyanate (*Chem. Soc. Trans.*, 1885, 770). *Diphenylene diisocyanate*, $CO:N\cdot C_6H_4\cdot C_6H_4\cdot N:CO$, was obtained from benzidine hydrochloride and phosgene; on treatment with alcohol it is converted into *diphenylene diurethane*, $COOEt\cdot NH\cdot C_6H_4\cdot C_6H_4\cdot NH\cdot COOEt$, which may also be prepared from benzidine and ethylic chloroformate; the corresponding phenylated urethane is obtained by the interaction of phenol and diphenylene diisocyanate.

Metatoluylene diamine and phosgene react to form metatoluylene diisocyanate, which is converted by phenol into the carbamate, $Me\cdot C_6H_3(NH\cdot COOPh)_2$.

No cyanate was formed on heating orthotoluylenediamine with phosgene; both this diamine and orthophenylenediamine, however, react with ethylic chloroformate to form urethanes.

On heating phenyl hydrazine at 220—230° in an atmosphere of carbonyl chloride, a solid compound of phenyl cyanate with hydrogen chloride was formed.

18. "The Oil obtained from Lime-leaves." By Francis Watts.

The fragrant yellow oil of the lime-tree (*Citrus limetta*) obtained by distilling the leaves and young shoots in a current of steam, contains a citrene, $C_{10}H_{16}$, boiling at 178—179°, and methylnonyl ketone; it appears also to contain "terpinol." On distillation about one-half boils above 280° and has the appearance of colophene.

ADDITIONS TO THE LIBRARY.

I. Donations.

Anleitung zur qualitativen chemischen Analyse, von C. R. Fresenius. Fünfzehnte neu bearbeitete und verbesserte Auflage. Braunschweig, 1885: from the Author.

A Practical Introduction to Chemistry; by W. A. Shenstone, London, 1886: from the Author.

Spectrum Analysis; six Lectures delivered in 1868 before the Society of Apothecaries of London; by Sir H. E. Roscoe. Fourth Edition, revised and enlarged by the author and by A. Schuster. London, 1885: from the Author.

Annales de Chimie, Tomes LV—LX; Paris, 1805-6:
from Dr. J. H. Russell, F.R.S.

Transactions of the South African Philosophical Society. Vol. III, Part 2, 1883-5. Cape Town, 1885: from the Society.

Fourth Annual Report of the Board of Control of New York Experimental Station, for the year 1885. Rochester, U.S., 1886:
from the Board.

Titles of papers of interest to chemists recently read before Societies in the United Kingdom:—

"The Injurious Effect of a Blue Heat on Steel and Iron." By C. E. Stromeyer.
Institution of Civil Engineers, January 29th.

"Proteïd Substances in Latex." By J. R. Green, B.A., B.Sc.

"On Intravascular Clotting." By L. C. Wooldridge, M.B., D.Sc.

"Observations on the Radiation of Light and Heat from Bright and Black Incandescent Surfaces." By Mortimer Evans, M.I.C.E.
Royal Society of London, Jan. 14th, Feb. 4th and 18th.

1. "Chemical Affinity and Solution." By W. Durham.

2. "On the probable Heats of Formation of Zinc-Copper Alloys," By A. P. Laurie.

3. "On the Mean Free Paths in a Mixture of Two Systems of Spheres." By Professor Tait.
Royal Society of Edinburgh, February 15th.

At the next meeting, on March 4th, there will be a ballot for the election of Fellows, and the following papers will be read:—

"The Influence of Temperature on the Heat of Chemical Combination." By S. U. Pickering.

"The Action of Heat on the Salts of Tetrethylphosphonium." By N. Collie.

"A New Method for the Preparation of Tin Tetrethyl." By N. Collie and Professor Letts.

SALE OF THE "ABSTRACTS OF PROCEEDINGS."

The Council having resolved to place the "Abstracts of Proceedings" on sale at a price of *7s. 6d.* per annum, intending subscribers and Fellows who desire to purchase extra copies are requested to apply without delay to Mr. Van Voorst, Paternoster Row, London, E.C.

NOTICE TO AUTHORS OF PAPERS.

To facilitate the preparation of these "Abstracts of Proceedings," all authors are requested to furnish abstracts of their communications, and to send their papers so that they may be in the hands of the Secretaries, if possible, on the Monday before the day of meeting.

ERRATUM.

Page 102, line 18 from top, *for* "9318" *read* "9738."

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 19. Session 1885-86.

March 4th, 1886. Dr. Hugo Müller, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. Carl Bennert, Ph.D., Blaydon, near Newcastle; Edwin Ebenezer Burnett, 118, Huddleston Road; Arthur Robert Ling, 14, Woburn Place, Russell Square, W.C.; Frank Morel, Aldersgate Chemical Works, Southall; Dr. Robson Roose, 45, Hill Street, Berkeley Square, W.

The following were elected Fellows of the Society:—Messrs. James Henry Allan, Henry K. G. Bamber, Leopold Mandeville Deane, Preo Loll Dey, Adolph Dresel, Herbert Samuel Elworthy, John William Ellis, Caleb Ferrey, M.B., B.Sc., James Arthur Formoy, Francis W. L. Glenfield, Bertram Harvey Hart, Andrew Henderson, George Thomas Holloway, Arthur Percy Hoskins, William Lang, Jun., Arthur Pillans Laurie, Peter MacEwan, Walter Newton, Eugene Obach, Oliver Quibell, James Galbraith Ross, Richard Spencer, Arthur John Starey, Francis Napier Sutton, Charles Metford Thompson, Julius Wertheimer, Sidney Williamson, Edward Willmore, William T. Wright and Brougham Young.

19. "A New Element: Germanium." By Clemens Winkler.

The author, in a letter addressed to the Society, dated Freiburg, Saxony, February 21st, 1886, states that he has discovered in the mineral *Argyrodite* a new non-metallic element, closely related to arsenic and antimony, and that he has named it *Germanium*.

Argyrodite is a new mineral discovered at Freiburg by A. Weisbach, consisting of silver, sulphur and germanium.

20. "The Influence of Temperature on the Heat of Chemical Combination." By S. U. Pickering.

A large number of experiments have been made by the author, with

the view of ascertaining whether the heat of combination is independent of temperature, or whether, if not, the variations are of a regular nature. According to Kopp's determinations of specific heats, the heat of combination of solids should be uninfluenced by temperature, but the methods available for ascertaining specific heats would be too imperfect to show any alterations in the heat of combination unless these were very great. The particular cases selected were the heat of hydration of a salt and the heat of formation of double salts. The sulphates were the salts chosen.

Every means was adopted for rendering the experiments as precise as possible; the temperatures employed were confined within the ordinary range of atmospheric temperatures; as many as seven different thermometers were used, the more delicate of which read to less than 1/3000° C., and a method was devised whereby the same portion of any instrument was used for every experiment with any particular substance, whatever the temperature might be. The proportion of salt to water taken was 1 : 400 formula weights with the single sulphates, and 1 : 800 with the double sulphates.

Hydrates in Solution.—The results when plotted as curves exhibit very remarkable features. In no case is the heat of dissolution of any of the salts represented by a straight line nor even by a single curve, but consists of a series of curves more or less regular in their nature.

Hydrated potassium magnesium sulphate exhibits the greatest number of such changes; a straight line may be drawn so as to touch or nearly touch the portions of the curves at 2·5°, 7·5°, 15° and 22·5° C., the portions intermediate between these points corresponding about 100 calories above this straight line. Hydrated magnesium sulphate exhibits similar peculiarities, but fewer in number, the points of minimum heat evolution being about 3°, 14° and 22° C. With hydrated copper sulphate the heat of dissolution appears to be represented by a series of straight lines rather than curves. Hydrated potassium copper sulphate presents the appearance of one curve, broken only by a deep indentation extending from 12·5° to 15°. With hydrated sodium sulphate there is a depression between 5·5° and 10·5°, the heat of dissolution above this point being probably represented by a straight or nearly straight line.

The curves of the anhydrous salts generally exhibit peculiarities resembling those of the corresponding hydrated salts, but not always. With potassium sulphate there is a break at 14°, a similar one occurs with lithium sulphate, but in the case of sodium sulphate such a break is absent. The curves of these three salts do not show any marked resemblance.

The increase in the heat of dissolution of a salt which thus takes place at certain temperatures, can only be attributed, in the author's

opinion, to the formation of some new and higher hydrate. That an increase of temperature should favour the formation of such is not considered extraordinary, when it is remembered that the temperatures at which the observations were made are comparatively low, and that with sodium sulphate, where we have other reasons for considering a high temperature would favour the dissociation of the salt from its water, no such increase takes place after 10·5°, a much lower temperature than in any other case. No special changes were noticed at 4° C., the temperature of the maximum density of water. The author considers that the heat of formation of these higher hydrates is probably not an inconsiderable quantity in comparison to that of the known hydrates of the salt, but it is impossible to determine its exact value in any special case.

The occurrence of these successive changes in the constitution of a salt in solution will involve successive variations in the specific heat of their solution; the temperature of the latter, therefore, will rise under the influence of a constant source of heat, not in a regular but in an undulatory manner.

Water of Crystallisation.—A comparison of the heat of dissolution of the same salt in the hydrated and anhydrous condition gives the heat of formation of the solid hydrated salt. When the various values obtained for this at different temperatures are represented diagrammatically, they form a series of curves showing that the heat of this combination is not a constant quantity. With magnesium sulphate the heat of hydration increases from 13,100 cal. at 3° to 13,300 cal. at 23°, there being a small but questionable break at 14° C. With copper sulphate the variation is much more marked; the line forms one curve from 2° to 9°, another from 9° to 17°, after which it again rises, attaining the value of 11,320 cal. at 23°, whereas at 2° it was only 10,780 cal. The heat of hydration of the double salts shows similar irregularities as well as a similar tendency to increase with the temperature. With sodium sulphate only is a decrease in value observed as the temperature rises, this decrease beginning at about 15°, after experiencing some remarkable fluctuations at lower temperatures.

These fluctuations in the heat of hydration of a salt the author attributes to intramolecular rearrangements; changes of a nature similar to those which cause the same substance, sometimes even when an element, to exhibit different physical and chemical properties. The general tendency towards an increase in the heat of combination as the temperature rises is in accordance with what has already been observed in other cases.

From these variations in the heat of hydration it follows that the specific heat of a solid hydrated salt will be subject to small variations, as in the case of its solution, and also that it will not be exactly equal

to the sum of the specific heats of the anhydrous salt and water, but generally slightly less.

It is observed that the temperature at which the heat of hydration of a solid salt is a minimum corresponds to an increased heat in the dissolution of the hydrated salt, as if the possibility of a higher hydrate being formed were due to there being less energy expended in retaining the water already combined.

Double Salts.—The heat of formation of the double salts, $MgSO_4,K_2SO_4$ and $CuSO_4,K_2SO_4$, in the solid and anhydrous condition, was calculated from the data already alluded to. This quantity appears to vary also with the temperature; with both salts it attains a minimum at about 14°, the extreme variation with the copper compound being as much as 640 cal., from − 240 cal. to + 400 cal. One of the most remarkable features in the variation of this quantity is that an increase in it occurs at those temperatures which are marked by a *decrease* in the heat of combination of the same double salt with its water of crystallisation, thus bearing out the conclusions previously drawn from a comparison of this latter quantity with the heat of dissolution, as to there being some principle of intramolecular compensation, whereby an increase in the energy of combination between any two portions of a molecule can take place only at the expense of the energy between these and the other portions.

21. "The Salts of Tetrethylphosphonium and their Decomposition by Heat." By Professor E. A. Letts and Norman Collie, Ph.D.

The authors confirm Hofmann's statement that *tetrethylphosphonium hydroxide* is resolved on heating into ethane and triethylphosphine oxide; the change occurs quantitatively. The *chloride*, PEt_4Cl, is resolved quantitatively into triethylphosphine hydrochloride and ethylene. On heating the *carbonate* they obtained triethylphosphine together with its oxide, and diethylketone, carbon dioxide and tetrane, whereas Hofmann and Cahours state that it yields triethylphosphine and ethyl carbonate. The *acid carbonate* behaves similarly. The *acetate* appears to undergo two distinct changes, and to be resolved partly into triethylphosphine oxide and methylethylketone, and partly into triethylphosphine, carbon dioxide, ethylene and methane. The *benzoate* is decomposed in a similar manner, ethylphenylketone and benzene taking the place of ethylmethylketone and methane. The products of decomposition of the *oxalate* at 200—230° are triethylphosphine and its oxide, ethylene, carbon monoxide and dioxide, and perhaps diethylketone. If the oxalate be heated to 160° with the minutest trace of sulphur, a deep indigo-blue colour becoming green and finally yellow is produced; this reaction furnishes an excellent

test for sulphur. The *sulphate* yields almost quantitative amounts of triethylphosphine sulphide and oxide, together with charred products. A concentrated solution of the *cyanide* decomposes when heated, and yields triethylphosphine oxide, ethane and hydrogen cyanide; a small quantity of what appears to have been propionitrile was also obtained. The *iodide* decomposes in a complex manner and yields charred products.

22. "The Formation of Acids from Aldehydes by the Action of Anhydrides and Salts, and the Formation of Ketones from the Compounds resulting from the union of Anhydrides and Salts." By W. H. Perkin, Ph.D., F.R.S.

The method of preparing unsaturated acids from aldehydes discovered by the author has of late been the subject of much discussion, Fittig especially contending that condensation takes place between the aldehyde and the *salt*, and not, as the author supposes, between the aldehyde and the *anhydride*. Believing the arguments put forward by those who oppose this latter interpretation to be inconclusive, he has resumed the study of the subject; the experiments are as yet incomplete, however, and only one observation bearing on the question is fully discussed in the paper. The author has previously shown that when a mixture of isobutyric anhydride, sodium isobutyrate and benzaldehyde is heated, carbon dioxide and butenylbenzene are produced; these result from the decomposition of phenylhydroxyisobutyric acid, which Fittig has proved to be the first product of the reaction. He now finds that on heating a mixture of benzaldehyde, isobutyric anhydride and an acetate, about 60 per cent. of the theoretical amounts of butenylbenzene and carbon dioxide are obtained; whereas, on employing acetic anhydride and sodium isobutyrate, cinnamic acid was obtained in considerable quantity, and less than half as much carbon dioxide and butenylbenzene as in the previous experiments. These results afford strong evidence that condensation takes place between the aldehyde and the anhydride, and not between the aldehyde and the salt.

The paper mainly consists of an account of the results obtained on heating anhydrides with their salts. On boiling a mixture of butyric anhydride and sodium butyrate, carbon dioxide is gradually evolved and dipropylketone is formed. Isobutyric anhydride and sodium isobutyrate react in a similar manner. A mixture of sodium propionate with excess of propionic anhydride, heated in sealed tubes at 180—190°, yields carbon dioxide and diethylketone; and acetone is obtained in like manner from acetic anhydride and an acetate. The author believes that the formation of the ketone depends on the inter-

action of the salt and the anhydride, and that this is the case appears to be proved by the observation that methylpropylketone is obtained if a mixture of sodium acetate and butyric anhydride be heated.

23. "A New Method of Preparing Tin Tetrethide." By Professor E. A. Letts and Norman Collie, Ph.D.

In preparing zinc ethide by Gladstone and Tribe's method, the authors obtained a liquid bye-product which they ultimately ascertained was tin tetrethide. Experiments were therefore made with zinc-tin alloys containing from 1 to 50 per cent. of tin; the yield of tin tetrethide, calculated as percentage of tin converted, varied from 27—56 per cent., but in most of the experiments about 50 per cent. of the tin present was converted, whatever the composition of the alloy. The yield of tetrethide was almost proportional to the mass of tin in the alloy until it contained one-third tin; it then became almost inactive, and the time necessary to complete the reaction increased enormously. On adding powdered tin to the zinc-copper couple together with ethyl iodide, tin tetrethide was produced on heating; and a similar result was obtained when zinc ethiodide was heated with powdered tin, but it was necessary to raise the temperature to 160°. Alloys of zinc with 20 per cent. antimony, aluminium, bismuth and lead, when heated with ethyl iodide, gave only zinc ethide.

24. "Contributions to the History of Cyanuric Chloride." By Alfred Senier, M.D.

On heating together cyanuric chloride, $C_3N_3Cl_3$, and sodium acetate in closed tubes at 100°, sodium cyanurate, $C_3N_3O_3Na_3$, and acetyl chloride are produced, but interaction takes place only partially. Silver acetate is not attacked by the chloride; and cyanuric acid and acetic anhydride do not act on each other. On heating sodium formate with cyanuric chloride, sodium cyanurate, carbonic oxide and hydrogen chloride are formed. Sodium benzoate and cyanuric chloride give benzoyl chloride and sodium cyanurate, 88 per cent. of the theoretical yield of the former being obtained. The action of cyanuric chloride on benzamide is similar to that of phosphorus pentachloride, and results in the formation of cyanuric acid, benzonitrile and hydrogen chloride. *Benzoyl cyanurate*, $C_3N_3(C_7H_6O_2)_3$, is readily obtained on heating a mixture of benzoyl chloride and silver cyanurate at 100°; it is readily hydrolysed, if heated for a short time with water at 100°, into benzoic and cyanuric acids.

25. "The Action of Naphthylamine on Cyanuric Chloride." By Harold H. Fries.

The author has succeeded in displacing the three chlorine-atoms in cyanuric chloride one by one by the group $NH{\cdot}C_{10}H_7$. The dichloride, $C_3N_3Cl_2(NH{\cdot}C_{10}H_7)$, and the monochloride, $C_3N_3Cl(NH{\cdot}C_{10}H_7)_2$, are obtained on mixing the proper quantities of cyanuric chloride and naphthylamine, both dissolved in ether; they crystallise from hot alcohol in needles, the former melting at 149°, the latter at 215°. When either of these bodies is heated with the proper quantity of amine at 100°, *naphthylmelamine*, $C_3N_3(NH{\cdot}C_{10}H_7)_3$, is formed; it melts at 223°.

26. "Sulphine Salts containing the Ethylene Radicle. Part I. Diethylenesulphide-methyl-sulphine Salts." By Orme Masson, M.A., D.Sc.

Two substances of the empiric formula C_2H_4S have been described, one being an amorphous insoluble non-volatile compound, concerning whose constitution nothing is known; the other is crystalline, dissolves in alcohol, ether and carbon disulphide, boils at 200°, and, as Husemann has shown, has a vapour-density corresponding to the formula $(C_2H_4)_2S_2$. The author describes the preparation of this latter; he then discusses its constitution, showing that it is adequately represented by the formula $S\left\{\begin{matrix}C_2H_4\\C_2H_4\end{matrix}\right\}S$.

This sulphide unites directly with methyl iodide to form *diethylene-sulphide-methyl-sulphine iodide*, $S\left\{\begin{matrix}C_2H_4\\C_2H_4\end{matrix}\right\}S\left\{\begin{matrix}CH_3\\I\end{matrix}\right.$.

A series of derivatives prepared from this iodide are described, viz.:—The iodide, $C_5H_{11}S_2I$; the tri-iodide, $C_5H_{11}S_2I_3$; the nitrate, $C_5H_{11}S_2NO_3$; the silver salt, $C_5H_{11}S_2NO_3{\cdot}AgNO_3$; the sulphate, $2(C_5H_{11}S_2)_2SO_4{\cdot}7H_2O$; the chloride, $C_5H_{11}S_2Cl$; the chloroplatinates, $(C_5H_{11}S_2Cl)_2PtCl_4$, $(C_5H_{11}S_2Cl)_4 3PtCl_4$, $(C_5H_{11}S_2Cl)PtCl_4$, $C_{10}H_{21}S_4Pt_2Cl_9$); the gold salt, $C_5H_{11}S_2Cl{\cdot}AuCl_3$; the mercury salt, $C_5H_{11}S_2Cl{\cdot}HgCl_2$; the hydroxide, $C_5H_{11}S_2OH$; a volatile oil, $C_{12}H_{24}S_5$.

In their general characters the salts of the base resemble those of trimethyl-sulphine, but they differ in some important particulars, of which the following are the most striking:—

1. There is much less tendency to form addition-products with the halogens.

2. The salts are decomposed by potash.

3. The hydroxide undergoes a peculiar decomposition, slowly when cold, rapidly on heating; the chief product of which is the oil $C_{12}H_{24}S_5$.

4. The compounds formed by the chloride with platinic chloride are peculiarly various, and are possessed of characteristic properties.

5. None of the salts examined, with the exception of the sulphate, are at all deliquescent.

The constitution proposed by the author for this sulphine base represents it as trimethyl-sulphine in which two methyl-gronps are displaced by the dyad (comparatively negative) group $S(C_2H_4)_2$. This view of their constitution affords an explanation of the first two of the above-mentioned characteristics of the base.

27. "Sulphine Salts containing the Ethylene Radicle. Part II. On Dehn's Reaction between Ethylene Bromide and Alkyl Sulphide." By Orme Masson, M.A., D.Sc.

In 1865 Dehn published an account of the action of ethylene bromide on ethyl sulphide (*Annalen*, Suppl. IV, 83), which he summed up in the following scheme :—

$$(1.)\ 2C_2H_4Br_2 + 2(C_2H_5)_2S = (C_2H_4)_2S_2 + 4C_2H_5Br.$$
$$(2.)\ C_2H_5Br + (C_2H_5)_2S = (C_2H_5)_3S.$$
$$(3.)\ C_2H_4Br_2 + (C_2H_5)_2S = (C_2H_5)_2(C_2H_4)S^{vi}Br_2.$$
$$(4.)\ C_2H_4Br_2 + C_2H_4S = (C_2H_4)_2S^{vi}Br_2.$$

The truth of equations (1) and (2) was well proved; that of (3) and (4) rested on rather doubtful evidence.

If the compounds $(C_2H_5)_2(C_2H_4)S^{vi}Br_2$ and $(C_2H_4)_2S^{vi}Br_2$ really exist, they are unique specimens of a class of sulphin*ic* salts, and are of considerable theoretic interest. An investigation, however, of the circumstances attending the formation of the salts to which Dehn attributed these formulæ, of the properties of their platinum salts (as described by Dehn), and of the analyses on which this theory was based, conclusively shows that Dehn was really dealing with salts analogous to those described by the author in Part I of this communication. The author supports this conclusion by proving that sulphine salts possessed of the required properties are actually formed when diethylene disulphide is heated with ethyl bromide and with ethylene bromide. He therefore substitutes the following equations for Dehn's third and fourth :—

$$(3.)\ C_2H_5Br + (C_2H_4)_2S_2 = C_2H_4)_2S_2(C_2H_5)Br.$$
$$(4.)\ C_2H_4Br_2 + (C_2H_4)_2S_2 = \{(C_2H_4)_2S_2\}_2(C_2H_4)Br_2.$$

28. "The Identity of Certain Mixed Ethereal Oxalates." By L. Gordon Paul.

The author has compared the methylic ethylic oxalate obtained, 1, by adding the theoretical amount of $CH_3{\cdot}OH$ to the chloride

COCl·COOEt, and 2, by adding the theoretical amount of C_2H_5·OH to the chloride COCl·COOMe, and concludes that the two reactions furnish the same product. If an excess of alcohol be used, methylic oxalate in the one case, and ethylic oxalate in the other, is obtained in place of the mixed salt; but whereas the displacement of ethyl by methyl takes place at once and is very complete, that of ethyl by methyl is much more gradual and less complete. Methylic oxalate may be converted into ethylic oxalate by heating it with methylic alcohol, and *vice versâ*. Methylic ethylic oxalate is converted by repeated distillation into a mixture of methylic and ethylic oxalates.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Third Annual Report, 1881–82, of the Bureau of Ethnology of the Smithsonian Institution: by J. W. Powell, Director: Washington, 1884: from the Institution.

Journal of the Iron and Steel Institute: No. II, 1885: London, 1885: from the Institute.

Outlines of Organic Chemistry: by H. F. Morley: London, 1886: from the Author.

The Chemistry of the Coal-tar Colours: by R. Benedikt: translated and edited, with additions, by E. Knecht: London, 1886: from the Publishers.

An Introduction to Practical Organic Analysis: by G. E. R. Ellis: London, 1885: from the Author.

Rudiments of Chemistry: by Temple Orme: London, 1886: from the Publishers.

Annual Report for 1885 of the Comptroller of the Currency of the United States: Washington, 1885: from the Comptroller, H. W. Cannon.

Bulletin of the United States Geological Survey: New Series: Nos. 7–14.

II. *By Purchase.*

Micro-organisms and Disease; an Introduction to the Study of Specific Micro-organisms: by E. Klein: London, 1885.

The Dyeing of Textile Fabrics: by J. J. Hummel: London, 1885.

Sugar Growing and Refining: by C. G. W. Lock, G. W. Wigner, and R. H. Harland: London, 1885.

A Treatise on the Principles of Chemistry: by M. M. P. Muir: London, 1884 (for Reference Library).

Annuaire de l'Observatoire de Montsouris pour l'an 1886: Paris, 1886.

Papers of interest to Chemists recently read at Societies in the United Kingdom:—

"Note on the Paper by Mr. J. W. Clark on the Determination of the Heat-Capacity of a Thermometer." By A. W. Clayden.

"On Experimental Errors in Calorimetrical Work: and on Delicate Calorimetrical Thermometers." By S. U. Pickering.

Physical Society, January 23rd and February 13th.

"On Radiant Matter Spectroscopy. Note on the Earth Yx." By W. Crookes, F.R.S.

"Colour Photometry," By Captain Abney, R.E., F.R.S., and Major-General Festing, R.E.

Royal Society of London, February 25th and March 4th.

"On the Magnitude of the Mutual Attraction between two pieces of Matter at distances of less than 10 micro-millimètres." By Sir William Thomson.

"On Radiation from Snow." By John Aitken.

"On the Change of Volume of a Salt when Dissolved in Water." By J. H. Pollok.

"On Electrolytic Polarization." By W. Peddie.

"On Thermometer Screens." By J. Aitken.

Royal Society of Edinburgh, March 1st.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 20. Session 1885-86.

March 18th, 1886. Dr. Hugo Müller, F.R.S., President, in the Chair.

Messrs. A. Dresel, Albert Ivatt and Edward Willmore were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Cosmo Innes Burton, 11, Upper Phillimore Gardens, W.; Arthur William Clayden, North Lodge, Bath College, Bath; Christopher Hodgson, 144, Blake Street, Barrow-in-Furness; John William King, St. George's Hospital, W.; Henry Oliver Minty, 731, Wandsworth Road, S.W.; Richard Lloydd Whiteley, University College, Nottingham.

The following papers were read:—

30. "Note on the Combustion of Cyanogen." By Harold B. Dixon, M.A.

A few years ago, on discovering that a spark might be sent through a well-dried mixture of carbonic oxide and oxygen without causing explosion, the author made several experiments on well-dried cyanogen and oxygen. These experiments seemed to show that cyanogen, like carbonic oxide, would not explode when dry. On returning to this investigation last autumn, the author discovered that the non-explosion of cyanogen previously observed was due not to the absence of moisture, but to the insufficient temperature of the spark. A spark 1 mm. long from a Voss machine may be passed through a mixture of cyanogen and oxygen without causing explosion or any appreciable decomposition of the cyanogen. A mixture of the gases dried by standing in contact with anhydrous phosphoric oxide for two months exploded with violence when a strong spark was passed through it. A similar mixture which had stood in contact with a stick of potash also exploded violently.

It was found that the initial rate of explosion of carbonic oxide and oxygen increased rapidly with the amount of aqueous vapour present in the mixture; similar experiments made with cyanogen and oxygen showed that the initial rate of explosion diminished on adding aqueous vapour. It seems evident, therefore, that the explosion of cyanogen and oxygen does not depend upon the presence of water, which merely acts as a diluent in the mixture.

The author has shown that when a platinum wire is raised to redness in a well-dried mixture of carbonic oxide and oxygen, the wire glows intensely for a short time, and that complete combination takes place between the carbonic oxide and oxygen without visible flame. A precisely similar phenomenon is observed when a platinum wire is raised to full redness in cyanogen and oxygen: the wire glows brightly and the cyanogen is oxidised to carbon dioxide. The tube is filled with orange vapour both when the oxygen is present in excess and in defect, but to a smaller extent in the latter case. No flame is visible round the glowing coil of wire. When the wire is only raised to dull redness no action seems to take place; on breaking the circuit the wire cools immediately; but when once the action has begun, the wire continues glowing half a minute after the circuit is broken.

Discussion.

The President remarked that it appeared to him that the cause of this remarkable behaviour of cyanogen just brought under the notice of the Society depended probably not so much on the greater heat effect of the larger or rather the longer spark as on its greater potential energy, which starts the explosive wave, for it is generally supposed that the degree of temperature in a small spark is much the same as that of a larger one of the same electromotive force.

Dr. Armstrong said that the study of the behaviour of mixtures of cyanogen and oxygen in comparison with that of mixtures of carbonic oxide and oxygen, was of peculiar interest, as cyanogen was one of the few gases which decomposed with evolution of heat. It was well known that a certain minimum electromotive force was required to electrolyse liquids, and to effect the electrolysis of gases a minimum —relatively very high—electromotive force was doubtless also required: an explanation of Mr. Dixon's observations might perhaps be based upon this circumstance.

31. "Note on the Constitution of the Naphthalene-derivatives." By R. Meldola.

Having been unable to attend the meeting of the Society when Mr. Stallard read his paper on the bromophthalic acids published in

the current number of the Journal (p. 187), I may take this opportunity of pointing out that the new proofs advanced by him in favour of the constitution $CO_2H : CO_2H : Br = 1 : 2 : 3$ for the bromophthalic acid of m. p. 174—176° appear to me to be perfectly conclusive. The same conclusion has, in fact, been simultaneously arrived at by Guareschi (*Atti d. R. Accad. d. Sci. d. Torino*, vol. xxi, January 24th, 1886), who has obtained a chlorophthalic acid of m. p. 124° (anhydride, m. p. 124—125·5°) by the oxidation of γ-dichlornaphthalene. The constitution of this chlorophthalic acid is analogous to that of the bromophthalic acid obtained by Smith, Guareschi and myself, and the isomeric acid of Alèn, which has the constitution $CO_2H : CO_2H : Cl = 1 : 2 : 4$, and melts at a lower temperature (148° according to Alèn; 130—134° according to Krüger).

In accordance with this evidence, it becomes necessary to modify the formula of Guareschi's nitrobromonaphthalene (m. p. 122·5°) as proposed by Mr. Stallard, and as the discoverer has himself pointed out in the paper referred to. The formula given by me in my last paper (Trans., 1885, 513) for the dibromonaphthylamine of m. p. 105° must also be corrected, and I may here point ont that the constitution of this substance and of its derived di- and tri-bromonaphthalenes can be now definitely established. The corrected formulæ will be—

Dibromonaphthylamine, m. p. 105°, $Br : Br : NH_2 = 1' : 1 : 3$
Dibromonaphthalene, m. p. 74°, $Br : Br = 1 : 1'$
Tribromonaphthalene, m. p. 110°, $Br : Br : Br = 1 : 1' : 3$.

The alternative formula $Br : Br : NH_2 = 1' : 4 : 2$ for the dibromonaphthylamine is excluded, because it does not give γ-dibromonaphthalene on displacing the NH_2-group by H.

The dibromonaphthylamine of m. p. 101—102° (Trans., 1885, 514) must accordingly have the constitution $NH_2 : Br : Br = 1 : 3 : 3'$ or $1 : 3 : 2'$, but there is at present no evidence to decide which of these formulæ is correct. That the second Br-atom does not occupy an α-position in the unsubstituted nucleus appears from the fact that I failed to obtain the 1 : 2 : 3 bromophthalic acid from it by oxidation. Further, as this dibromonaphthylamine gave only a slight trace of phthalic acid when oxidised, it would appear that the second Br-atom does not enter the substituted nucleus. Unfortunately, I have not enough of the dibromonaphthylamine left to repeat the oxidation experiment, but I find on reference to my laboratory notes that the oxidation was twice performed with different preparations and with the same result in each case. The minute quantity of phthalic acid formed certainly does not appear to me sufficient to establish the formula $Br : Br : NH_2 = 3 : 2 : 1$, which is the only other one admissible (Trans., 1885, 514).

The chief discrepancy at present remaining to be cleared up is the apparent identity of the two dibromonaphthalenes of m. p. 74°. I have re-examined the specimens in my possession, and as far as melting point and crystalline form can be trusted as indications of identity, these two dibromonaphthalenes are certainly indistinguishable from one another; nevertheless they may be isomeric, as I have already pointed out (Trans., 1885, p. 516) that naphthalene derivatives which are known to be isomeric may have the same crystalline form and melting point. The question can only be decided by a further study of the derivatives of the dibromonaphthalenes in question, but I regret that the quantity at my disposal is much too small to enable me at present to extend the research in this direction. The bromophthalic acid used by H. v. Pechmann (*Ber.*, **12**, 2126) may have been the meta-compound, the production of erythroxyanthraquinone from the corresponding bromobenzoylbenzoic acid being due to intramolecular migration to the ortho-position on fusion with alkali.

I may take the present opportunity of pointing out that the dibromonaphthalene (m. p. 68°) obtained by Canzoneri (*Gazzetta*, **12**, 424) from Smith's monobromo β-naphthol, is in all probability identical with the orthodibromonaphthalene described in a former paper (Trans., 1883, 5). It has been argued that the investigations of Beilstein and Kurbatow (*Annalen*, **202**, 228) show that β-dinitronaphthalene (m. p. 176°) has both NO_2-groups in the same benzene-ring, most probably in the meta-position (Jacobson, *Inaug. Diss.*, 1882, 37). If so, ζ-dichloronaphthalene (m. p. 83°), obtained by Atterberg (*Ber.*, **9**, 1730) by the action of PCl_5 upon this dinitronaphthalene, is analogous to the metadibromonaphthalene (m. p. 64°) described by me in 1879 (*Ber.*, **12**, 1962).

Discussion.

Dr. Armstrong said that as regards the constitution of β-dinitronaphthalene, the production from it of *dinitrophthalic acid* (Beilstein and Kurbatow) by the action of nitric acid in sealed tubes, was not satisfactory evidence; and Jacobson's contention that Liebermann and Dittler's nitro-α-naphthol (m. p. 128°) could not well be an ortho-derivative because the amidonaphthol prepared from it did not furnish a quinone on oxidation was equally unsatisfactory as being negative evidence; there was no obvious flaw in Atterberg's argument that ζ-dichloronaphthalene is an α-α-derivative (*Watts' Dictionary*, vol. viii, Pt. II, p. 1376). The argument from analogy is apt to break down on comparing benzene with naphthalene, as two new "laws" come into force in the case of naphthalene, namely, the tendency for substitution to take place in both "rings," and the marked tendency to form α-derivatives. The formula given by

Professor Meldola to the dibromonaphthylamine melting at 101—102° must be accepted with reserve on this latter account.

32. "Action of Ammonia on Chromyl Dichloride." By Samuel Rideal, B.Sc.

Dry ammonia gives with chromyl dichloride ammonium chloride, nitrogen and brown oxide of chromium, the reaction being expressed by the equation: $3CrO_2Cl_2 + 8NH_3 = 6NH_4Cl + N_2 + Cr_2O_3{\cdot}CrO_3$. No addition products or chromammonium bases are formed when the vapour of chromyl dichloride burns in an atmosphere of dry ammonia under the ordinary temperature and pressure. This explanation of the reaction agrees with the observation of Persoz that 20·98 parts of chromyl dichloride absorb 79·1 parts of ammonia.

33. "Note on the Estimation of Resin in Soaps." By C. R. Alder Wright, D.Sc., F.R.S., and C. Thompson, F.C.S.

We have had occasion to make a number of experiments with various of the methods hitherto proposed for the determination of resin in soaps, with the general result of finding that one and all leave much to be desired in the way of accuracy. Sutherland's process (oxidation by nitric acid) in some instances gave fair results; but this occurs mostly through the balancing of two opposite sources of error, viz., incomplete removal of resin by oxidation—tending to *increase* the percentage of fatty acid found; and oxidation of true fatty acids—tending to *decrease* it. Treatment of aqueous soap solution by various processes intended to throw out of solution true soaps of fatty acids leaving dissolved resinates did not answer at all well in our hands: sometimes fatty soaps were retained in solution, and resinates were often mechanically carried out of solution along with the fatty soaps, and no certainty of complete separation was ever attainable.

On the whole, the process recommended by Gladding (*Chem. News*, April 14, 1882) seemed to give figures most in accordance with the truth, provided the nature of the fatty matters contained in the soap examined were approximately known so as to permit of the application of a correction-factor variable to some extent with this nature. The method consists in separating the fat acids, dissolving about 0·5 gram in 95 per cent. alcohol, neutralising with saturated alcoholic potash, then adding a few additional drops and boiling to saponify any small quantity of glyceride present (through imperfection in manufacture, &c.); after cooling, ether is added to 100 c.c., and finely powdered *neutral* silver nitrate, and the whole well agitated: finally a known fraction of the ethereal solution of

silver resinate, &c., is treated with hydrochloric acid, and the liberated resin, &c., weighed after evaporation of the ether. According to Gladding (who, however, only quotes a very small number of test experiments), 100 c.c. of alcoholic ether dissolves 23·5 mgrms. of oleic acid, when "pure fat acid" (mixture of stearic and oleic?) is thus treated; and this correction-factor he found to be applicable with accuracy when Castille soap, linseed oil soap and soaps containing known amounts of resin were examined.

Our experience, however, is that 23·5 mgrms. (representing 4·7 per cent. on 0·5 gram fatty acids and resin) is a correction-factor by no means universally applicable. With pure stearic or oleic acid it is much too large: with acids from castor-oil far too small; with various mixtures it is not far from the truth. Thus the values given in the table were obtained as the result of a large number of observations which, moreover, did not always show a high degree of concordance, notwithstanding all the care taken to avoid sources of error; partly no doubt this is due to the circumstance that different specimens of oils, &c., were employed in the production of the soaps treated. The temperature was throughout not far from 18° C., but was not kept absolutely uniform; which circumstance may again partly account for apparent irregularity in the solubility of the silver salts.

Although Gladding's correction of 23·5 mgrms. is not strictly applicable in all cases, yet the figures in the table indicate that it is not far from the truth in at least a number of instances of mixtures likely to occur in actual manufacture: in such cases a tolerably fair approximation to the truth is attainable by assuming that the weight of the resin apparently found in 0·5 gram of fatty acids should be diminished by some 25 mgrms., or what is the same thing, that the percentage of resin found in the total fatty acids, &c., is 5 per cent. too high. But this correction cannot be regarded as applicable universally.

Nature of fatty matters in soap examined.	Fatty matters dissolved (as silver salt) in 100 c.c. of alcoholic ether.		
	Maximum.	Minimum.	General average.
	mgrms.	mgrms.	mgrms.
Pure stearic acid	16·0	8·0	11·6
„ oleic „	15·0	9·0	12·0
Nearly pure palmitic acid	30·0	28·0	29·1
Cotton-seed oil	34·0	20·0	26·9
Castor oil	62·0	49·0	53·9
Cocoanut oil (fatty acids dried on water-bath)	17·5	12·0	14·8
Cocoanut oil (fatty acids dried over H_2SO_4)	23·0	19·0	21·1
Stearic and oleic acids, in nearly equal proportions	22·0	18·0	19·1
Stearic acid and cotton-seed oil, in nearly equal proportions	—	—	25·5
Oleic acid and cotton-seed oil, in nearly equal proportions	—	—	24·5
Stearic acid and cocoanut oil (water-bath), in nearly equal proportions	—	—	23·4
Oleic acid and cocoanut oil (water-bath), in nearly equal proportions	—	—	25·6

A source of error that should not be overlooked is that the concentrated alcoholic potash used as directed by Gladding is liable on keeping to become dark-coloured, and in so doing to contain more or less notable amounts of resinoid matter (from action on the alcohol or impurities contained therein). Several milligrammes of increment in the ether residue may readily be brought about by the use of such potash solution. Another source of error is the decomposition of certain of the insoluble silver salts of fatty acids by light, causing in some instances appreciable amounts of additional matter to become dissolved in the alcoholic ether.

34. "The Properties of the Nitrobenzalmalonic Acids." By Charles M. Stuart, M.A.

On boiling benzalmalonic acid, $C_6H_5{\cdot}CH : C(COOH)_2$, with water, it is resolved partly into benzaldehyde and malonic acid (1), and partly into cinnamic acid and carbon dioxide (2); the three nitro-derivatives behave similarly, the percentage amounts converted in accordance with the first and second modes of change being shown in the following Table.

	Boiled for 1 hour.			Boiled for 15 min.		
	I.	II.	Total.	I.	II.	Total.
Benzalmalonic acid.....	85·2	—	—	57·8	1·41	59·2
,, ,, ...	85·8	10·8	96·6	58·3	1·25	59·5
,, ,, ...	84·4	10·6	95·0	—	—	—
Paranitrobenzalmalonic acid	80·2	14·8	95·0	61·54	3·89	65·4
,, ,, ...	82·7	12·4	95·1	62·64	3·77	66·4
Metanitrobenzalmalonic acid	83·1	10·4	93·5	61·3	6·3	67·6
,, ,, ...	79·9	14·4	94·3	62·5	5·8	68·3
,, ,, ...	79·7	12·6	92·3	—	—	—
Orthonitrobenzalmalonic acid	24·5	5·7	30·2	8·7	1·18	9·88
,, ,, ...	23·6	6·5	30·1	8·71	1·25	9·96
,, ,, ...	24·4	6·4	30·8	—	—	—

Benzalmalonic acid and its para- and meta-nitro-derivatives form additive compounds with bromine and with hydrogen bromide, which are decomposed by water. The ortho-nitro-derivative is converted both by the action of bromine and hydrogen bromide into a condensation product which is not decomposed by water or alcohol. The author suggests that this behaviour may be regarded as an argument in favour of Kekulé's benzene formula.

From cinnamic acid and malonic acid he has obtained a phenylbutindicarboxylic acid, $C_6H_5{\cdot}CH:CH{\cdot}CH:C(CO_2H)_2$; this melts at 208°, but is resolved into CO_2 and cinnamenylacrylic acid.

Salicylic and malonic acids give coumarincarboxylic acid; this melts at 187° without decomposing, but is resolved at a higher temperature into CO_2 and coumarin.

The Anniversary Meeting of the Society will take place on Tuesday, March 30th, at 8 P.M.

At the next ordinary meeting, on Thursday, April 1st, the following papers will be read :—

"The Determination of Boiling Points." "The Action of a Red Heat on Chloroform." By Prof. Ramsay and Dr. Young.

"The Use of the Electric Light to Influence Chemical Change." By Dr. Armstrong.

"Some Sulphur Compounds of Barium." By V. H. Veley.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 21. Session 1885–86.

March 30th, 1886. Annual General Meeting. Dr. Hugo Müller, F.R.S., President, in the Chair.

The President delivered an address, of which the following is an abstract :—

The number of Fellows of the Society is now 1459, 31 of these being honorary foreign members. 111 new Fellows have been elected since the last Anniversary Meeting; 8 Fellows have withdrawn, 19 have been removed on account of arrears, and 16 have died, viz., one honorary foreign member, Prof. Hermann von Fehling, and Frederick Allen, Prof. Andrews, F.R.S., E. O. Brown, G. W. H. Clements, Frederick Field, F.R.S., James Higgin, Rev. S. Morris, James Parette, Thomas Spencer, Dr. E. G. Schweitzer, Surgeon-Major Sheppard, Henry Shepheard, Alfred Tribe, Dr. John Smith, W. S. Ward and Walter Weldon, F.R.S.

104 papers have been communicated to the Society during the year: this is not only a great advance upon the previous year, when the number was 67, but is the largest number hitherto attained with the one exception of 1880–81, when the number read was 113. The last number of Transactions is consequently one-third larger than that of the previous year. The President is inclined to think that this increased activity is due in no inconsiderable degree to the fact that the various new laboratories which have been established in the country during the last few years are now gradually entering upon their full duties; and he is of opinion that we may look forward with confidence to a continuous and steadily increasing development in the pursuance of scientific chemical work in this country.

New bookcases have been filled up at the Society's expense during the year, and thus considerable additional space has been secured for the library.

The subject catalogue of the library has just been issued to Fellows. The Council are greatly indebted to Professor McLeod, F.R.S., and to

Mr. Warington for the assistance they have rendered in preparing this catalogue, as well as to the Librarian, Dr. Thorne.

After dwelling on the recent incorporation of the Institute of Chemistry by Royal Charter, the President expressed his gratification at being able to testify to the manifest progress in the activity of the Society and to the otherwise prosperous condition of its affairs; in conclusion he proceeded to discuss briefly the conditions which affect the cultivation of scientific chemistry in this country.

It was then moved by Dr. Gladstone, and seconded by Professor Thorpe, that the thanks of the meeting be given to the President for his address, and that he be requested to allow it to be printed. Referring to the publication of the catalogue, Dr. Gladstone said that in looking through it he felt that it not only gave information as to what was, but also what was not, in the library, and it might well serve to lead many of us to make suggestions and to help to fill up gaps from our own shelves. The resolution was unanimously accepted, and was acknowledged by the President.

The Treasurer, Dr. Russell, then read his report, giving an explanation of the balance sheet. He said that the funds of the Society were in a satisfactory state, the income for the year having been £3743 and the expenditure £3108, leaving a balance in hand of £635, a sum that would make it possible to fund the life compositions received during the year.

Mr. Carteighe moved that the thanks of the Society be tendered to the Treasurer for his services during the past year; this was seconded by Mr. Friswell.

Mr. Crookes proposed a vote of thanks to the auditors, which was seconded by Professor Clowes; Mr. Makins replied.

A vote of thanks to the Officers and Council having been proposed by Mr. H. B. Dixon, seconded by Mr. Pickering, and acknowledged by Dr. Armstrong,

Mr. Howard moved that the thanks of the meeting be given to the Editor, Sub-editor, Abstractors and Librarian for their important services to the Society during the year; this was seconded by Mr. J. A. R. Newlands. Mr. Groves and Dr. Thorne replied.

Professor Humpidge and Dr. Teed were appointed scrutineers, and a ballot having been taken, the following were declared elected Officers and Council for the ensuing year:—

President: Dr. Hugo Müller.

Vice-Presidents who have filled the office of President: Sir F. A. Abel; Dr. Warren De La Rue; Prof. Frankland; Dr. J. H. Gilbert; Dr. J. H. Gladstone; Professor A. W. Hofmann; Professor W. Odling; Dr. W. H. Perkin; Sir Lyon Playfair; Sir H. E. Roscoe; Professor A. W. Williamson.

Vice-Presidents: Mr. W. Crookes; Professor J. Dewar; Mr. David Howard; Professor G. D. Liveing; Professor T. E. Thorpe; Professor W. A. Tilden.

Secretaries: Dr. H. E. Armstrong; Mr. J. Millar Thomson.

Foreign Secretary: Dr. F. R. Japp.

Treasurer: Dr. W. J. Russell.

Ordinary Members of Council: Messrs. H. T. Brown; Professor T. Carnelley; M. Carteighe; Professor Frank Clowes; A. E. Fletcher; R. J. Friswell; Professor R. Meldola; R. Messel; J. A. R. Newlands; S. U. Pickering; Professor W. Ramsay; Thomas Stevenson.

April 1st, 1886. Dr. Hugo Müller, F.R.S., President in the Chair.

Certificates were read for the first time in favour of Messrs. Holland Crompton, 15, Belgrave Road, St. John's Wood, N.W.; George William Saul Hudson, Church Street, Settle, Yorkshire; A. Wentworth Jones, Godington Rectory, near Bichester; William Henry Pendlebury, B.A., Christ Church, Oxford.

The following papers were read:—

35. "The Determination of Boiling Points." By Professor Ramsay and Sydney Young, D.Sc.

Professor Ramsay called attention to the device employed by Dr. Young and himself in determining boiling points (*Phil. Trans.*, 1884, p. 471), which consists in encasing the thermometer bulb in cotton-wool or asbestos; in distilling a pure liquid, the temperature remains constant throughout owing to the presence of a film of liquid on the thermometer bulb.

Discussion.

Professor Ramsay, in reply to a question by Dr. Japp, said that he was of opinion that in distilling mixed liquids the liquid of higher boiling point very rapidly expels that of lower boiling point from the wool, and that hence the proper temperature is indicated almost immediately.

36. "The Vapour-pressures of Bromine and Iodine, and Iodine Monochloride." By Professor Ramsay and Sydney Young, D.Sc.

After calling attention to the extremely discrepant statements as to the melting and boiling points of bromine and iodine, the authors describe their own observations.

Bromine.—The statements of various authors and books vary enormously, the melting point of bromine being given as — 7·3° by Regnault and as — 25° by Liebig, its boiling point being stated as 58° by Andrews and 63° by Pierre—these being extreme values.

Two samples of bromine were examined by the authors after being submitted to purification. The melting point directly observed was between — 7·0° and —7·45°, and from their results generally they infer that it is very near to — 7·05°; the boiling point of the first sample was 57·65° at 749·8 mm. pressure, that of the second was 58·85° at 755·8 mm., but they incline to think that the latter contained some impurity—perhaps a brominated carbon compound, and give as the corrected number 58°.

Iodine.—The melting point of iodine was observed to be between 113·8° and 114·1°, and they regard 114·15° as the true number; the boiling point under 760 mm. pressure was found to be 184·61°.

It was found impossible to obtain useful numbers for iodine monochloride on account of its instability.

Discussion.

The President remarked that the great discrepancies between many of the earlier determinations of the physical constants of bromine were probably due to the presence of bromine carbon compounds.

Mr. Groves said that the boiling point given by Mr. Bolas and himself (59·6°) was determined by using about 2 lbs. of very carefully purified bromine, which certainly contained very little, if any, carbon tetrabromide.

37. "The Use of the Electric Light to Influence Chemical Change." By Henry E. Armstrong.

It is well known that many chemical changes take place under the influence of light which do not occur under otherwise identical conditions in its absence. Schramm's recent experiments have proved that light has a most remarkable effect in influencing the direction of change in cases in which action takes place very readily both in presence and absence of light: thus whereas when chlorine acts on toluene in the dark chlorotoluenes are formed, in sunlight benzyl chloride is produced; ethyl benzene is excessively sensitive, bromethylbenzene, instead of ethylbromobenzene, being obtained by the action of bromine even in diffused light, and if the treatment be continued in sunlight the dibromide, $C_6H_5{\cdot}CBr_2{\cdot}CH_3$, is produced, whereas cinnamene bromide, $C_6H_5{\cdot}CHBr{\cdot}CH_2Br$, is formed if bromine be allowed to act on heated bromethyl benzene; in sunlight, pseudocumene is at once converted into the monobromide, $C_6H_3Me_2{\cdot}CH_2Br$,

and more slowly into the dibromide, $C_6H_3Me(CH_2Br)_2$, whereas mono-, di-, and tri-bromopseudocumene are formed in absence of light. Dr. Armstrong finds that, as was to be expected, the light of the electric arc may be substituted for sunlight. The influence of light may therefore be readily exhibited as a lecture experiment, as the product of the action of bromine in darkness on pseudocumene after removal of hydrogen bromide has no action on an alcoholic solution of silver nitrate, whereas the product obtained under the influence of light at once reacts with such a silver solution. It is merely necessary to drop the bromine into the hydrocarbon in a flask directly exposed to the rays from the arc. Owing to the uncertainty of sunshine, the complex arrangements which are necessary if it is to be used for any lengthened period, and the variation in its intensity, it is conceivable that the use of a powerful electric arc may be of considerable advantage in experiments on the influence of light in promoting or controlling chemical change and even in some manufacturing operations.

38. "Some Sulphur Compounds of Barium." By V. H. Veley, M.A.

It is shown by the results both of synthetical and analytical experiments that the monohydrate of barium hydroxide is converted into barium monosulphide in accordance with the equation $Ba(OH)_2,H_2O + H_2S = BaS + 3H_2O$; known weights of the hydroxide were taken, and a certain weight of the sulphide and of water obtained.

By the action of hydrogen sulphide on an aqueous solution of barium hydroxide, a solution of barium hydrosulphide is formed from which crystals of the composition $Ba(SH)_2,4H_2O$ separate out; this substance is far more stable than the corresponding calcium compound. The evolution of hydrogen sulphide is concomitant with that of water; when all the latter has been given off the retention of hydrogen sulphide by the anhydrous substance is most marked: only at a red heat is all the hydrogen sulphide given off and the conversion of the hydrosulphide into the sulphide complete.

A warm saturated solution of barium hydrosulphide dissolves sulphur to give a red liquid, from which crystals of barium tetrasulphide, $BaS_4{\cdot}2H_2O$, separate.

Barium hydroxyhydrosulphide absorbs carbon disulphide with formation of an unstable barium thiocarbonate.

Discussion.

Prof. Ramsay said that Mr. Veley's account reminded him that years ago on dissolving sulphur in a solution of barium hydroxide,

after crystallising out the thiosulphate, he obtained crystals like those described by Mr. Veley, but of the formula BaS_7.

Mr. Veley, in reply to Dr. Messel, said that he had examined the product made on a large scale by roasting barium sulphate with coal, &c., and had found the crystals to consist of barium hydroxyhydrosulphide with a slight excess of SH_2.

Dr. Teed added that he had always found barium and sulphur present in these crystals in the ratio Ba : S.

39. "Parabenzylphenol and its Derivatives and a New Benzylphenol." By Prof. E. H. Rennie, M.A., D.Sc.

Dinitroparabenzylphenol has been further examined (comp. Trans., 1882, **33**, 220); if gently warmed with concentrated nitric acid, it is converted into the trinitro-derivative, but on boiling it with the slightly diluted acid the smell of benzaldehyde is noticed and it is converted into trinitrophenol.

The oily residue left after purification of parabenzylphenol yields a sulphonic acid isomeric with that from parabenzylphenol; its potassic salt crystallises with $2\frac{1}{2}OH_2$. This salt is converted into a nitrosulphonate by nitric acid, and into a bromosulphonate by bromine; the nitrosulphonate is converted by nitric acid into an isomer of dinitroparabenzylphenol, and into a bromonitrobenzylphenol by bromine.

Discussion.

Dr. Armstrong said that the formation of trinitrophenol from dinitrobenzylphenol was analogous to that of dinitrobromophenol from bromonitrobenzylphenol; it was noteworthy that Prof. Rennie had described this latter reaction in 1882, although Widmann in his recent paper (*Ber.*, 1886, 278) speaks of the displacement of an alkyl radicle by NO_2—in the conversion of cumenylacrylic into paranitrocinnamic acid—as altogether without precedent. Prof. Rennie and he, in a communication to the Society in March 1883, had shown that the supposed trinitrothymol was in reality trinitrometacresol; the formation of this latter body from dinitrothymol was a reaction precisely similar to that described by Widmann.

40. "Amidodiphenylsulphonic Acid and Azo-dyes from Diphenyl." By Thos. Carnelley, D.Sc., and James Schleselman.

p-*Amido-diphenylsulphonic acid*, $C_{12}H_8(NH_2)\cdot SO_3H$. Only one acid of this composition appears to be obtained by the action of strong sulphuric acid on *p*-amido-diphenyl (m. p. 49°) at a temperature of 130°. It is practically insoluble in cold and but very slightly soluble

even in boiling water. The *sodium salt*, $C_{12}H_8(NH_2)\cdot SO_3Na + 2H_2O$, and the *barium salt*, $[C_{12}H_8(NH_2)\cdot SO_3]_2Ba + 4H_2O$, are described.

The following azo-compounds prepared from the acid are described :—

Sodium phenol-p-*diazodiphenylsulphonate*, $HO\cdot C_6H_4\cdot N_2\cdot C_{12}H_8\cdot SO_3Na$.
This dyes wool and silk a beautiful yellow.

Sod. resorcinol-p-*diazodiphenylsulphonate*, $(HO)_2\cdot C_6H_3\cdot N_2\cdot C_{12}H_8\cdot SO_3Na$.
This dyes silk, wool, and raw jute a beautiful orange.

Sod. quinol-p-*diazodiphenylsulphonate*, $(HO)_2\cdot C_6H_3\cdot N_2\cdot C_{12}H_8\cdot SO_3Na$.
This dyes silk and raw jute a very pretty golden-amber.

Sod. α-naphthol-p-*diazodiphenylsulphonate*, $HO\cdot C_{10}H_6\cdot N_2\cdot C_{12}H_8\cdot SO_3Na$.
This dyes silk, wool, and raw jute a deep reddish-brown.

Sod. β-naphthol-p-*diazodiphenylsulphonate*, $HO\cdot C_{10}H_6\cdot N_2\cdot C_{12}H_8\cdot SO_3Na$.
This dyes silk, wool, and raw jute a brilliant red.

Discussion.

Professor Meldola remarked that a number of dyes were now prepared from benzidin (diamidodiphenyl), which were of considerable technical importance: Congo red was one of the most valuable.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

A Short Manual of Chemistry: by A. Dupré and H. W. Hake: Vol. I. Inorganic Chemistry: London, 1886: from the Authors.

Memoranda of the Origin, Plan, and Results of the Field and other Experiments conducted on the Farm and in the Laboratory of Sir John Bennet Lawes, Bart., LL.D., F.R.S., at Rothamsted, Herts: also a Statement of the Present and Previous Cropping, &c., of the Arable Land not under Experiment: June, 1885: from Sir J. B. Lawes, Bart.

Merchant Venturers' School, Bristol: Preliminary Prospectus: Bristol, 1885.

A Manual of Metallurgy: by W. H. Greenwood: Vol. 1. Fuel, Iron, Steel, Tin, Antimony, Arsenic, Bismuth, and Platinum: London and Glasgow, 1885: from the Author.

Catalogue of the Library of the Pharmaceutical Society of Great Britain: London, 1885: from the Society.

II. *By Purchase.*

Sur les Alcaloïdes derivés de la Destruction Bacterienne ou Physiologique des Tissus Animaux: Ptomaïnes et Leucomaïnes: By E. J. A. Gautier: Paris, 1886.

Die Chemische Natur der Mineralien: von C. F. Rammelsberg: Berlin, 1886.

Titles of Papers of interest to Chemists recently read at meetings of Societies in the United Kingdom:—

"On the Explosion of Homogeneous Gaseous Mixtures." By Dugald J. Clerk, F.C.S.

Institution of Civil Engineers, March 7th.

"On the Volumetric Estimation of Inorganic Nitrites." By G. Armstrong Atkinson.

"The Absolute Determination of the Strength of an Electric Current by means of the Balance." By Professor Blyth.

"On Sulphines." By Orme Masson.

"On the Nature of the Relationship of Urea Formation to Bile Secretion." By D. Nöel Paton, M.B., C.M.

Royal Society of Edinburgh, March 15.

"On an Apparatus for Connecting and Disconnecting a Receiver under Exhaustion by a Mercurial Pump." By Professor J. T. Bottomley.

"Comparative Effects of Different Parts of the Spectrum on Silver Salts." By Captain Abney, F.R.S.

"On the Properties of Matter in the Gaseous and Liquid States under various Conditions of Temperature and Pressure." By the late Dr. Thomas Andrews, F.R.S.

"Electrolytic Conduction in Relation to Molecular Composition, Valency, and the Nature of Chemical Change; being an Attempt to apply a Theory of 'Residual Affinity.'" By Professor H. E. Armstrong, F.R.S.

Royal Society of London, March 18th and 25th.

HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY, ST. MARTIN'S LANE.

ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 22. Session 1885-86.

April 15th, 1886. Dr. Hugo Müller, F.R.S., President, in the Chair.

Mr. H. R. G. Bamber was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Edwin Jennings Ball, Ph.D., 15, Trafalgar Square, Chelsea, S.W.; Parvathi Nath Datta, 5, West Newington Place, Edinburgh; Robert Elliot Doran, Bray, Co. Wicklow; Richard Dormer, Garstan; William Edward Dawson, Pretoria, Transvaal, South Africa; William Dobinson Halliburton, 135, Gower Street, W.C.; John Tysilis Johnson, Glyn Hof, Conway; William Selby Simpson, 95, Darenth Road, Stamford Hill, N.; Henry H. Walker, 35, St. Tham Road, Fulham, S.W.

The following were elected Fellows of the Society:—

Messrs. E. E. Burnett; Cosmo J. Burton; Carl Bennert, Ph.D.; Arthur W. Clayden; Christopher Hodgson; John W. King; Charles Kilpatrick; Arthur R. Ling; Henry O. Mintz; Frank Morel; Robson Roose; Richard Ll. Whiteley.

Mr. R. J. Friswell exhibited a very large specimen of metatolylenediamine, $C_6H_3Me(NH_2)_2$.

The following papers were read:—

41. "The Eurhodines, a New Class of Colouring Matters." By Otto N. Witt, Ph.D.

By acting with orthoamidoazo-compounds on α-naphthylamine hydrochloride, new dye-stuffs may be obtained, which have received

the name of *Eurhodines*. The typical eurhodine, prepared from amidoazotoluene and α-naphthylamine, crystallises in orange needles. Its solution in ether is yellow, and shows a brilliant green fluorescence. Its salts are of a scarlet colour. The formula of eurhodine is $C_{17}H_{13}N_3$. By the action of acids it is transformed into eurhodol, $C_{17}H_{12}N_2O$, whilst ethylic nitrite produces the ethylic ether of eurhodol, $C_{17}H_{11}N_2OC_2H_5$. Eurhodine is recognised as amidonaphthylenetoluquinoxaline. A large number of eurhodines may be obtained synthetically by the action of orthodiketones on triamines which have two of the amido-groups in the ortho-position. The substance $C_{20}H_{13}N_4$ formed by the action of phenanthraquinone on 1 : 2 : 4 triamidobenzene has been examined and found to resemble closely the typical eurhodine. The joint oxidation of orthotoluylenediamine and α- and β-naphthol has been studied. α-Naphthol produces a blue dye belonging to the indophenol-group, while β-naphthol gives rise to the formation of a new naphthylenetoluquinoxaline. As only two of these are capable of existence, the new compound must be the β-β-isomeride.

42. "The Action of Sodium on Ethereal Salts of Phenylacetic Acid." Part II. By W. R. Hodgkinson.

In this communication the author principally draws attention to the solid substance produced in small quantity by the action of sodium on ethylic phenacetate (phenylacetate) to which reference was made in the previous paper (Trans., 1880, 480).

The products of the reaction were stated to be ethylic acetate; an oil to which the formula $C_{18}H_{20}O_3$ was provisionally given; phenylacetic acid; and the solid body in question. The reaction was represented as occurring between 6 mols. phenacetate and 2 atoms of sodium; but it is difficult to dissolve so large a proportion of sodium without heating too strongly, and it is better to use 8 mols. phenacetate to 2 atoms of sodium.

On examining larger quantities of the oil to which the formula $C_{18}H_{20}O_2$ was given, the author finds that it is not a uniform substance: it decomposes into substances of high boiling point—water being given off—even when distilled under reduced pressure. If the crude product be hydrolysed by means of alcoholic potash, it yields phenacetic acid and a more stable oil; this oil principally consists of a substance which boils at 320—325°, and has the composition of dibenzylketone: such a ketone would result from the hydrolysis of ethylic phenacetophenacetate, $Ph{\cdot}CH_2{\cdot}CO{\cdot}CHPh{\cdot}COOEt$.

The solid substance produced simultaneously with the oil is represented by the formula $C_{24}H_{18}O_3$. It is not an acid, although it is obtained in solution apparently in the form of a sodium-derivative on

heating the crude product of the action of sodium with water; but it is easily precipitated from this solution even by absorption of atmospheric carbon dioxide. It is almost insoluble in water, and has no action on test-paper; the aqueous solution, however, gives a deep-red coloration with ferric chloride. It dissolves in strong solutions of potassic carbonate without carbon dioxide being evolved, and also in dilute alcoholic potash; it slowly dissolves in sulphuric acid, and is reprecipitated by water if the acid be not heated. It reacts with ammonia and with hydroxylamine. It is unaffected by heating with water at 210°. It is oxidised with difficulty, and yields a product which is not an acid. It melts at 175°; the fused substance solidifies to a glassy mass which softens at 100° and then assumes a crystalline state, and melts as before at 175°.

The author is of opinion that this substance results from the occurrence of a reaction similar to that recently observed by Baeyer in the case of ethylic sodiomalonate, and that, in fact, it is a *triphenylphloroglucin*, $(C_6H_5)_3C_6H_3O_3$, three molecules of ethylic sodiumphenacetate condensing to form triphenyltrisodiophloroglucin, three molecules of alcohol being eliminated.

If sodium act at a temperature of 140—150° on an excess of ethylic phenacetate, ethylic phenacetophenylsodacetate is produced.

The author has also examined the action of sodium on the ethylic salts of the toluic acids: the para- and meta-compounds appear to undergo a complex decomposition, but the ortho-compound yields ethylic acetate and a ketone, $C_{14}H_{10}O$.

43. "The Action of Metals on Acids." By Henry E. Armstrong.

Our knowledge of the nature of alloys is at present very limited: it is supposed that some metals are capable of combining, but that others form mere mixtures, when fused together—the alloy being, as it were, "a solidified solution of the one metal in the other." This differentiation is based on the study of physical properties of alloys in comparison with those of the constituent metals. In certain cases—but these are very few in number—the actual composition of the compound may be deduced: thus in the case of the tin-copper alloys abrupt changes in electrical conductivity correspond to compounds of the formula $SnCu_4$ and $SnCu_3$, and the curve of conductivity for the tin-gold alloys also exhibits a striking series of maxima and minima from which the existence of definite compounds may be inferred. It appeared possible that, by dissolving alloys in a liquid capable of acting on both metals and determining the electromotive force between the alloy and a less positive metal, evidence of the existence of definite compounds might be obtained if the alloy dissolved as a whole. At

Dr. Armstrong's suggestion, a number of determinations of this kind have been made by Messrs. Holland Crompton and W. E. Sumpner, students of the Central Institution, but the investigation is as yet far from being completed: they have measured the E.M.F. between the alloys and platinum in nitric acid by means of an electrometer. The general result is that the method is inapplicable since the alloys do not as a rule behave as wholes. The E.M.F. observed in several cases is very nearly that between the less positive metal of the alloy and platinum, the more positive constituent dissolving independently and giving rise to a local circuit: thus in the case of copper-zinc alloys the E.M.F. is very nearly that of copper as long as the alloy contains not much less than about 5 per cent. of copper; the tin-zinc and tin-copper alloys also have an E.M.F. near to that of the less positive metal until alloys are reached containing but a small proportion of this constituent. In mercury-zinc alloys the more positive metal determines the electromotive force; this apparently is also true of the lead-tin alloys. Slight changes have been observed which, if confirmed by further experiments, are probably significant: thus in the tin-zinc alloys, the E.M.F. gradually rises from that of tin as the amount of this metal in the alloy diminishes: it is conceivable that this may be because the zinc acts as a diluent and separates the more complex tin molecules into simpler more active molecules. On the other hand, the E.M.F. of copper in bronze is slightly lower than that of pure copper, and that of copper in the copper-zinc alloys rich in zinc is also a little lower than that of pure copper; this may be due to the loss of energy in the formation of the alloy.

Dr. Armstrong then pointed out that although the method described was of little value, owing to the irregularity in the behaviour of alloys towards a solvent capable of attacking both metals, more was to be hoped from the employment of a solvent capable of acting upon only one, recent experiments by Mr. Laurie having shown that the E.M.F. between zinc-copper alloys and cuprous iodide in a solution of iodine and zinc iodide is about that of zinc until the alloy has the composition $CuZn_2$, when the E.M.F. suddenly falls to very nearly that of copper. Sodium and potassium exhibit a much lower E.M.F. when alloyed with mercury, according to Hockin and Taylor, and it is probable that the examination of a graduated series of their amalgams will afford indications of the composition of the compounds formed.

The E.M.F. between a given metal and platinum in nitric acid varies with the concentration of the acid. The following results were obtained with copper:—

Acid of rel. den. 1·5	E.M.F.	0·98 volt.
3 vols. 1·5 + 1 vol. 1·42.....	„	0·84 „
1 vol. 1·5 + 1 „ 1·42	„	0·63 „
„ 1·42	„	0·57 „
1 vol. 1·42 + 1 vol. water	„	0·75 „
1 „ „ + 3 „ „	„	0·81 „
1 „ „ + 7 „ „	„	0·81 „

These results appear to be entirely confirmatory of the conclusions already arrived at by Acworth and Armstrong (Trans., 1877), who found that the reduction of nitric acid was carried further—as indicated by the amount of nitrous oxide and nitrogen produced—when copper is dissolved in highly diluted nitric acid. The high E.M.F. observed on using the most concentrated acid is probably due to the fact that the initial product of reduction, nitrous acid, remains in solution. If the acid be less concentrated, the nitrous acid is more or less broken up ($3HNO_2 = 2NO + HNO_3 + H_2O$). The considerable rise in E.M.F. as dilution proceeds not improbably arises from the complex molecules of nitric acid being in part resolved into simpler more active molecules. The results also illustrate the importance of supplementing the chemical method of examining complex cases of change such as are involved in the action of metals on nitric acid by the electrical method. No appreciable action takes place during the time requisite to measure E.M.F., and therefore the solution remains practically unchanged in composition, whereas it is continuously changing during the entire course of a chemical experiment.

Referring to the action of metals generally on acids generally, Dr. Armstrong pointed out that it is probably impossible for the chemist to pronounce definitely in favour either of the modern view that the metal directly displaces the hydrogen of the acid, or of the older view that the metal displaces the hydrogen from water—the resulting oxide and the acid then interacting to form a salt; the decision of this question must apparently depend upon the determination of the nature of the phenomena during electrolysis of an acid solution. If the acid alone be the electrolyte, then doubtless the modern view is the correct one; but if both water and acid are electrolysed, and in proportions which vary according to the conditions, then both the old and new view of the nature of the action between a metal and the solution of an acid are correct, and the two kinds of change may go on side by side. The view put forward by Dr. Divers that silver, copper and mercury exercise an altogether peculiar action on nitric acid, "decomposing the nitric acid into hydroxyl and nitroxyl, and combining with these radicles to form

hydroxide and nitrite, which, by secondary reactions, become water, nitrous acid, and metal nitrate," does not appear to be compatible with the view that the interaction of a metal and an acid is essentially a case of electrolysis, there being no reason to suppose that nitric acid can be electrolysed into hydroxyl and nitroxyl, it is not supported by the observations here described on the E.M.F. of copper in acids of various strengths, which show that more depends on the state of the acid than on the metal; and, lastly, silver is incapable of acting on nitric acid, although it readily enters into interaction with the weaker electrolyte, nitrous acid.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Final Report of the Commissioners appointed to inquire into Accidents in Mines, and the possible means of preventing their occurrence or limiting their disastrous consequences: Folio, London, 1886: from the Commission.

Atomic Valency: by S. U. Pickering: London, 1866: (Pamphlet.)

II. *By Purchase.*

Travaux et Mémoires du Bureau International des Poids et Mesures: Tomes III and IV, 4to, Paris, 1884–5.

A Manual of Practical Hygiene: by E. A. Parkes: Edited by F. S. B. F. de Chaumont: 6th edition: London, 1883.

The Landmarks of Snake-poison Literature, being a Review of the more important researches into the nature of Snake Poisons: by V. Richards: Calcutta, 1885.

Gahrungs-Chemie für Pratiker: by J. Bersch. V. Die Schnell-Essigfabrikation: Berlin, 1886.

Neue Grundgesetze zur rationellen Physik und Chemie: von E. Dühring und U. Dühring: Zweite Folge: Leipzig, 1886.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 23. Session 1885-86.

May 6th, 1886. Dr. Hugo Müller, F.R.S., President, in the Chair.

Messrs. John W. King, William Herbert Hyatt and George T. Holloway were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. James Blake, M.D., F.R.C.S., 1, Sussex Gardens, W.; Forbes Rickard, Ashcombe, Carlton Road, Putney; Charles A. R. Jowitt, Scotia Works, Sheffield.

The following papers were read :—

44. "Paranitrobenzoylacetic Acid and some of its Derivatives." By Dr. W. H. Perkin, Jun., and Dr. E. Bellinot.

On account of the difficulty of producing ethylic benzoylacetate free from acetophenone, benzoic acid and other impurities, unsatisfactory results were obtained on attempting to prepare the nitro-derivative directly from it; the authors have therefore prepared *paranitrobenzoylacetic acid*, $NO_2 \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot COOH$, from paranitrophenylpropiolic acid obtained by combining ethylic paranitrocinnamate with bromine and treating the resulting ethylic paranitrophenyldibromopropionate with alcoholic potash. The conversion of paranitrophenylpropiolic acid into paranitrobenzoylacetic acid is effected by dissolving the former (50 grams) in 80—85 per cent. sulphuric acid (2—3 kilos.) and maintaining the liquid at 35—40° for 15 hours. The pure acid crystallises from benzene in microscopic needles; it melts at 135°, being resolved into paranitracetophenone and carbon dioxide, a decomposition which also takes place on boiling it with water. Owing to their instability, the preparation of its metallic salts is a matter of difficulty. *Methylic paranitrobenzoylacetate* crystallises from

alcohol in monoclinic prisms, melting at 106—107°; on treatment with sodium methylate or ethylate, it yields a monosodium derivative of remarkable stability. On heating this compound with benzyl chloride and a little alcohol in sealed tubes at 150°, it is converted into *methylic paranitrobenzoylbenzylacetate*, a body which crystallises from dilute alcohol in colourless plates, melting at 57°. *Ethylic paranitrobenzoylacetate* crystallises from a mixture of benzene and light petroleum in monoclinic prisms—of which, as well as of the methylic salt, measurements by Prof. Haushofer are given in the paper—melting at 75°; it dissolves fairly easily in sodic hydrate solution, being reprecipitated unchanged on the addition of acids. The sodium derivative may be obtained in a pure state by means of sodium ethylate: it crystallises from boiling alcohol in small orange-yellow needles, and may even be recrystallised from water; from it other metallic derivatives may readily be prepared.

Ethylic paranitrobenzoylethacetate, prepared by the action of ethyl iodide on the sodacetate, crystallises from dilute alcohol in colourless plates melting at 39—40°; the corresponding *allylacetate*, prepared by the action of allyl iodide, melts at 45—46°. All attempts to prepare the acids from these salts by hydrolysis were unsuccessful.

Ethylic diparanitrobenzoylsuccinate, $(C_6H_4{\cdot}NO_2)_2C_2H_2{\cdot}(COOEt)_2$, obtained by treating ethylic paranitrobenzoylsodacetate with iodine, crystallises from dilute alcohol in colourless needles melting at 180°. By the action of nitrous gas on an ethereal solution of ethylic paranitrobenzoylacetate, the *isonitroso*-derivative is obtained; it crystallises from dilute alcohol in colourless needles melting at 220°.

45. "An Acetic Ferment which forms Cellulose." By Adrian J. Brown.

The acetic ferment described in this paper is well known as the "vinegar plant" or "mother." Pure cultivations of it were made by a combination of the "fractional" and "dilution" methods, and also by growing it in a solid gelatin medium. The mode of growth of the tough gelatinous membrane of the ferment is described, its general appearance being very similar to a soft animal membrane. The membranous growth of the "vinegar plant" is the only form which it assumes, no matter how the conditions are varied. *Bacterium aceti* never assumes this form; moreover the "vinegar plant" gives all the chemical reactions of cellulose, but these are not yielded by any form of *B. aceti:* the two ferments are therefore specifically distinct. The morphology of the ferment is described, and also its fermentive actions. The latter, so far as examined, are similar to those of *B. aceti* (comp. Trans., 1886, 172), viz., ethylic alcohol is oxidised

to acetic acid, and the acid so formed is afterwards decomposed. Dextrose yields gluconic acid, and mannitol is converted into lævulose. Like *B. aceti* also, it had no fermentive action on cane-sugar or lævulose.

Treatment of a membrane of the "vinegar plant" by H. Müller's bromine method leaves a film of pure cellulose of the same shape and character as the original membrane. The reactions of this cellulose are given, showing it to be ordinary cellulose like that from cotton-wool.

The formation and use of cellulose by a simple cell plant is of interest in connection with the important part this body plays in the more highly organised plants. Experiments were therefore made to determine from what bodies the "vinegar plant" forms its cellulose. Cane-sugar, starch and ethylic alcohol are not converted into this body; dextrose, however, can be so converted. In this latter case, therefore, the cells of the ferment have a double action upon the sugar, viz., the production of gluconic acid and the building up of cellulose. The latter action, however, cannot be considered one of fermentation.

Mannitol and lævulose are converted into cellulose, and favour the growth of the ferment more strongly than dextrose.

The usual method of preparing "home made" vinegar by means of the "vinegar plant," is to introduce a membrane into a solution of cane-sugar. The pure ferment has no action on this sugar, but the ordinary impure ferment used contains yeast cells, and these invert and ferment the sugar, so preparing alcohol for conversion into vinegar by the acetic ferment.

The name *Bacterium xylinum* is suggested for the "vinegar plant."

Discussion.

Mr. Warington after noticing the remarkable formation of cellulose from lævulose, said that it would be important to ascertain, if possible, at what stage oxidation sets in. Recent experiments by Müntz clearly show that organisms may promote oxidations which cannot be of service to the life of the organism, and which, therefore, must be regarded as unessential thereto.

The President said that it had hitherto been always supposed that cellulose was the very foundation of all vegetable cells, and it was therefore particularly interesting to have it established that certain bacteria did not contain cellulose.

Titles of Papers of interest to Chemists recently read before Societies in the United Kingdom :—

"The Coagulation of the Blood." By Dr. L. C. Wooldridge.

"On an Effect produced by the Passage of an Electric Discharge through Pure Nitrogen." By Prof. J. J. Thomson, F.R.S., and Prof. R. Threlfall.

"Some Experiments on the Production of Ozone." By the same.

"Further Discussion of the most widened Lines in Sun-spot Spectra, observed at Kensington in 1879–85." By J. Norman Lockyer, F.R.S.

Royal Society of London, April 8th, May 6th.

At the next meeting, on May 20th, there will be a ballot for the election of Fellows, and the following papers will be read :—

"The Action of Aldehydes and Ammonia on Benzil" (*continued*). By Francis R. Japp, F.R.S., and W. Palmer Wynne, B.Sc.

"Imabenzil." By the same.

"Ammonia-derivatives of Benzoïn." By F. R. Japp and W. H. Wilson, Ph.D.

"Compounds of Benzil and Benzoïn with Alcohols." By F. R. Japp and Julius Raschen.

"The Action of Phosphoric Sulphide on Benzophenone." By the same.

"The Preparation and Saponification of Hydrocyanides of the Diketones." By F. R. Japp and N. H. J. Miller, Ph.D.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 24. Session 1885-86.

May 20th, 1886. Dr. Hugo Müller, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. Thomas Akitt, 25, Gascoyne Road, South Hackney, London; Alfred C. A. W. H. Chapman, 2, Queen Anne's Avenue, High Road, South Tottenham; Charles Alexr. Kohn, Redcliffe Villa, Redcliffe Road, Nottingham; John Temple Leon, 26, Belsize Park Gardens, N.W.; William Ray, Spenceley House, Victoria Road, Leeds; William Richards, 185, Isledon Road, Finsbury Park, London, N.; Joseph Price Remington, 1233, Walnut Street, Philadelphia, U.S.; William Saunders, London, Ontario, Canada; Charles A. Smith, The Laboratory, 8, Loftus Street, Sydney.

The following were duly elected Fellows of the Society:—Messrs. Edward Jennings Ball, Ph.D., Holland Crompton, Parvati Nath Datta, Robert Elliott Doran, Richard Dormer, Witham Dobinson Halliburton, George William Saul Howson, John Tysilio Johnson, A. Wentworth Jones, William Henry Pendlebury, William Selby Simpson, Henry H. Walker.

The President exhibited a specimen of the mineral Argyrodite—a sulphogermaniate of silver; also a number of specimens which he had recently received from Prof. Winkler of the new element Germanium (*ante*, p. 161) and its derivatives. He said that, according to the information given to him, germanium was a silver-white, brittle, volatile metalloid of the relative density 5·46; its atomic weight is 72·75. It appears to be identical with Mendelejeff's *Ekasilicium*, for which the atomic weight predicted was 72 and the relative density 5·5. Germanium forms two sulphides, a yellow monosulphide, soluble in alkali, which readily volatilises, subliming in well-formed crystals somewhat like those of iodine in colour; and a white

disulphide. It furnishes corresponding oxides: a liquid tetrachloride, boiling at 88°; and an orange-red, crystalline, volatile tetriodide.

Mr. Newlands called attention to the fact that in 1864 he had predicted the existence of an element having the atomic weight 73, and belonging to the carbon-silicon group.

Dr. Sprengel exhibited a series of specimens illustrating the effect produced on leaden cylinders by the explosion of equal weights (15 grams) of nitroglycerine and of mixtures of half nitric peroxide and half (*a*) CS_2, (*b*) benzene, (*c*) nitrobenzene, (*d*) nitrotoluene. The effect produced by the nitroglycerine was very much less marked than that produced by any of the other explosives, of which those containing nitrobenzene and nitrotoluene were by far the most powerful.

The following papers were read:—

46. "Sources of Error in the Calorimetric Study of Salts." By Prof. W. A. Tilden, F.R.S.

Mr. Pickering has recently published in the *Transactions of the Chemical Society* a paper containing very numerous estimations of the heat of dissolution of various salts at temperatures ranging from near zero to about 25° C., and in the *Phil. Mag.* for March and April he has given an account of the precautions he has taken to avoid experimental error or to make allowance for it.

In his principal paper (*Chem. Soc. Trans.*, May, 1886) he arrives at such extraordinary conclusions in regard to the behaviour of salts in act of dissolution in water, and at the same time protests so emphatically against the suspicion that the irregularities he has observed are due to experimental error, that having been myself occupied with experiments in the same direction, I have been led to examine Mr. Pickering's paper very carefully.

The process of dissolving a solid in water in such a manner as to allow of the determination of the heat evolved or absorbed is one which is beset with difficulties. But these are not all of equal importance, some being so small as to produce little or no appreciable effect on the result, others, however, being of such a formidable character as to render such determinations extremely difficult and uncertain. Mr. Pickering claims that his results exhibit an extremely high and altogether exceptional degree of accuracy. Without this exceptional accuracy the conclusion which he deduces cannot be maintained. A critical examination of the numbers recorded in his tables of results shows that his experiments, though undoubtedly conducted with great care and skill, have not led to results of any very unusual accuracy, and in fact that there are in many cases great discrepancies in the results of duplicate experiments. Some of these discrepancies I

attribute to a want of discrimination between the several sources of error in respect to their influence on the result.

Mr. Pickering has given great attention to the calibration and observation of his thermometers, even using instruments said to be capable of reading to $\frac{1}{3000}$th of a degree C., but he has given no detailed account of his method of correcting for the cooling or heating by radiation or conduction of the calorimeter during the progress of the experiment, although this latter, as he admits, is by far the most serious source of error, and might lead to a difference a hundred times greater than that arising from ordinary errors in calibration or reading of thermometers. Again, it would doubtless be impossible in such experiments to ensure the accomplishment of the act of dissolution in the several experiments at any given temperature in equal times; and yet if this is not done an error is introduced which it is impossible to estimate by observation of the rate of cooling before or after the experiment.

However, it is not suggested that Mr. Pickering's results are less than usually accurate, but only that they do not reach that unassailable standard which alone would justify the conclusions he draws from them. The supposition that the heat of dissolution of a given salt in water at successively higher temperatures is represented by a succession of irregular curves is not supported by Mr. Pickering's own experimental numbers, but results from the unjustifiable employment of arithmetical means. When *all* the numbers given in the tables are plotted on curve paper the remarkable sinuosities pointed out by Mr. Pickering for the most part disappear. One does perceive, however, that the discrepancies among the individual results are so great as to preclude the possibility of drawing from them any conclusion whatever as to the exact form of the curve in the several cases.

Discussion.

Mr. Pickering said that no one could be more fully aware than he was himself that the irregularities which he had observed depended on differences but little larger than those due to experimental error. The whole difficulty of the investigation lay in this very fact. No one could have laboured more energetically than he himself had done to disprove these irregularities, and he only accepted them when their existence became undeniable. In his opinion it was distinctly a case in which the means from a large number of experiments, and not each individual determination, should be considered. Taking the instances selected by Dr. Tilden, he contended that the irregularities could not be regarded as experimental errors. In the case of potassium sulphate the heat of dissolution from 26·5° to 17° is represented by a straight

line; from 11° down to 3° it is represented by another line at a different inclination from the first, but scarcely less straight. If the point at 14° is to lie in the first line the heat of dissolution there would be 6870 cals., if in the second line 6820 cals. Now of the eight determinations on which the observed depression at this point was based, the lowest was only 6908 cals.; the mean of four determinations with one thermometer gave 6941 cals., and of four other determinations with another thermometer 6963. By no possibility could Dr. Tilden manipulate those numbers so as to lower them even to 6870, and thus obliterate the depression which they represent. The only other means by which this could be done would be to admit an error of at least 82 cals. in the general results of all the other experiments —70 in number—at the other temperatures; a proposition quite inadmissible. Mr. Pickering professed himself ready to discuss in the same way the irregularities in any of the other curves. Dr. Tilden had specially alluded to the depression in the curve of $CuK_2(SO_4)_2{\cdot}6H_2O$, which was the one salt least fully examined of all; as Mr. Pickering had mentioned in his paper (p. 282), he would have paid but little attention to this depression were it not that there was subsidiary evidence that the point at which it occurs (14°) was a temperature at which the salt experienced some marked alteration. Looking at the curve representing the heat of combination of the salt with its water of crystallisation, it would be seen that this heat is represented by a straight line from 2° to 12° showing the rapid increase of 130 cals. per degree, while from 16° to 23° the heat of combination remains constant.

On the strength of there being but one determination with K_2SO_4 at 12·36°, Dr. Tilden accused him of having repeated experiments at the debatable points without having examined the points in its vicinity. This charge Mr. Pickering entirely denied. In the case in point Dr. Tilden would find on a more careful examination that within about 3° of the temperature where the depression was noticed (14°, there being eight experiments here) he had made no less than 19 determinations. Again, the lowest point (13·14°) in the $MgSO_4{\cdot}7H_2O$ curve, at which there were seven determinations, was accompanied by nine determinations at other temperatures within 1·5° of it. It was certainly natural, and indeed indispensable, that any point at which an anomaly was noticed should be more fully examined than other normal points, but the repetition of such experiments was generally accompanied by the repetition of other experiments at points above and below it, though not *necessarily* very near to it, and as a further precaution these experiments at different temperatures were in many cases, and at the expense of immense labour, performed on the same day (p. 281).

Dr. Tilden suggested that Mr. Pickering, while fully alive to the less important errors introduced by defects in the thermometers, might have overlooked the greater errors involved in determining the rate of cooling, and in the manipulation generally. Dr. Tilden would, however, find that in a paper read before the Physical Society (*Phil. Mag.*, 1886, p. 324) he had discussed not the errors inherent in thermometers, as he did in two other papers (*ibid.*, **180**, 330), but the errors of calorimetric work as illustrated by the actual results obtained in these very experiments themselves, results which had been influenced by and would therefore afford a criterion of the accumulated errors from all sources.

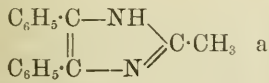
Mr. Pickering then described his method of operation, and explained that the determination of the rate of cooling was far more simple in his experiments than those of Dr. Tilden; for the temperature of the air is always the same as that of the calorimeter, and the rate of cooling was thus reduced so far as to be constant for the whole duration of the experiment. Mr. Pickering had found that even where the dissolution of a salt was not completed within five minutes or more, the final temperature of the calorimetric water was practically attained within about half a minute; it was during this short space of one half minute only that the temperature and therefore the cooling correction was uncertain.

Dr. Wright remarked that according to his experience the experimental error was much greater if the substances to be mixed were at the temperature of the air; the error due to radiation was much less if the temperature initially was as much below as it was finally above atmospheric temperature.

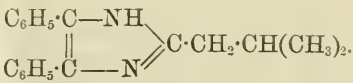
Prof. Tilden, in reply, said that he thought that Mr. Pickering had failed to explain the discrepancies which he had pointed out.

47. "On the Action of Aldehydes and Ammonia on Benzil." By Francis R. Japp, F.R.S., and W. Palmer Wynne, B.Sc.

The compounds obtained with acetaldehyde and isovaleraldehyde are the glyoxalines—



Methyldiphenylglyoxaline (m. p. 235°).



Isobutyldiphenylglyoxaline (m. p. 223°).

With cinnamaldehyde, benzil and ammonia, two reactions occur, two distinct compounds being formed, one of which is practically insoluble, the other moderately soluble, in boiling alcohol. The insoluble compound has the formula $C_{32}H_{28}N_2O_2$, and is an analogue

of that obtained by Japp and Hooker from salicylaldehyde, benzil and ammonia. It has the constitution—

$$\begin{array}{l} C_6H_5\cdot CH:CH\cdot CH\cdot NH\cdot CO\cdot C_6H_5 \\ \quad\quad\quad\

These formulæ have since been accepted by Henius (*Ann.*, **228**, 339).

In the note above referred to, Dr. Japp further admitted that the formula assigned by Henius to imabenzil was probably correct, basing this opinion upon an examination of *amorphous* imabenzil prepared by the method of Henius.

The authors have now prepared *crystallised* imabenzil, and have been able to rectify its formula, which they find to be $C_{35}H_{28}N_2O_3$. It is formed from benzil and ammonia according to the equation—

$$3C_{14}H_{10}O_2 + 2NH_3 = C_{35}H_{28}N_2O_3 + C_6H_5{\cdot}COOH + H_2O.$$

Imabenzil as prepared by Henius contains unaltered benzil. Contrary to the statement of Henius, imabenzil can be readily recrystallised; methyl alcohol was found to give the best results. The crystals have been measured by Mr. L. Fletcher, and found to agree with the description and approximate figure given by Laurent. The melting point was found at 194°.

49. "On Ammonia-derivatives of Benzoïn." By Francis R. Japp, F.R.S., and W. H. Wilson, Ph.D.

The action of alcoholic ammonia upon benzoïn was studied by Laurent and later by Erdmann. Both these chemists obtained a substance of the formula $C_{28}H_{24}N_2O$, to which Laurent gave the name *benzoïnam*. Erdmann further isolated a substance which he called *benzoïnimide*, assigning to it the formula $C_{14}H_{11}N$.

The authors confirm the formula of Laurent and Erdmann for benzoïnam. Their analyses of benzoïnimide, however, lead to the formula $C_{28}H_{20}N_2$. They regard it as an analogue of diphenanthrylene-azotide, $C_{28}H_{16}N_2$, and as it can no longer be classed as an imide, they propose to call it *ditolane-azotide*. It is most readily obtained free from the other compounds formed from benzoïn and ammonia, by heating benzoïn with fused ammonium acetate over a flame until the whole of the ammonium salt is volatilised.

A third compound, not described by the foregoing investigators, was obtained. It is formed in largest quantity when benzoïn is allowed to stand with alcoholic ammonia for several weeks in the cold. It crystallises from alcohol in minute oblique tables or prisms melting at 199°. The analyses agreed best with the formula $C_{28}H_{23}NO_2$. The equation for its formation would be $2C_{14}H_{12}O_2 + NH_3 = C_{28}H_{23}NO_2 + 2H_2O$. As nothing is known concerning its constitution, it may be named, for the sake of distinction, *benzoïnidam*.

50. "On Compounds from Benzil and Benzoïn and Alcohols." By Francis R. Japp, F.R.S., and Julius Raschen.

The authors have made experiments to ascertain whether other alcohols besides ethyl alcohol form condensation compounds with benzil in presence of a small quantity of caustic potash in the cold (comp. Trans., 1885, 90). Of the various alcohols employed only isopropyl alcohol yielded a result. A compound of the formula $C_{31}H_{28}O_4$ was obtained, which is deposited from alcohol in small lustrous faintly yellow crystals, of rhombohedral habit, melting at 147—148°. The benzil and isopropyl alcohol react according to the equation: $2C_{14}H_{10}O_2 + C_3H_8O = C_{31}H_{28}O_4 + O$, and the compound is therefore formed by a process of reduction, and is not analogous to the compound $C_{30}H_{24}O_4$, which, as was shown by Owens and Japp (*loc. cit.*), is formed from ethyl alcohol and benzil merely by elimination of water.

The action of a small quantity of potash at ordinary temperatures upon benzoïn dissolved in various alcohols was also tried, but only in the case of ethyl alcohol was a definite result obtained. Air must be carefully excluded during the reaction otherwise the benzoïn is oxidised to benzil. Benzoïn slowly reacts with ethyl alcohol, in presence of a small quantity of potash: $3C_{14}H_{12}O_2 + 2C_2H_6O = C_{46}H_{40}O_4 + 4H_2O$; the compound $C_{46}H_{40}O_4$ thus obtained corresponds with the compound $C_{46}H_{34}O_4$ formed by the interaction of the same molecular proportions of benzil and ethyl alcohol (*loc. cit.*). The benzoïn compound, $C_{46}H_{40}O_4$, melts at 249—250°.

51. "On the Action of Phosphoric Sulphide on Benzophenone." By the same.

By heating benzophenone with phosphoric sulphide for two days at 100° the authors obtained a compound $C_{26}H_{22}S_2$, melting at 152°, previously described by Engler, who prepared it both by the action of alkaline hydrosulphides upon benzophenonidene dichloride, $(C_6H_5)CCl_2$, and by heating benzhydrol with phosphoric sulphide.

At a temperature of 140—150° benzophenone and phosphoric sulphide yielded a compound of the formula $C_{26}H_{20}P_2S_5$. It crystallised from hot benzene in colourless microscopic plates melting at 226—227°. It decomposes in melting, assuming a deep-blue colour. It may be regarded as an ethereal thio-salt formed by the union of 2 mols. of thiobenzophenone, $(C_6H_5)_2CS$, with 1 mol. of phosphorous sulphide, P_2S_3. Its constitution may be expressed by the formula—

$$(C_6H_5)_2C<\overset{S}{S}>P\cdot P<\overset{S}{S}>C(C_6H_5)_2.$$

It would thus be a *benzophenonidene pyrothiophosphite*.

On oxidation with a solution of chromic anhydride in glacial acetic acid, it yields benzophenone.

52. "The Separation and Estimation of Zirconium by means of Hydrogen Peroxide." By G. H. Bailey, D.Sc., Ph.D.

The author has determined zirconium by means of hydrogen peroxide in a number of mixtures containing also iron, titanium and niobium, and finds that even when the zirconium forms only 2·3 per cent. of the mixture the method of separation which he has previously described (Trans., 1886, 149) is applicable and the results obtained are accurate. The zirconia precipitated in presence of a large excess of iron or of titanium does not contain a trace of these elements. The oxide generally obtained by means of hydrogen peroxide is the pentoxide, but he has also obtained a higher oxide, ZrO_3, apparently identical with that described by Cléve.

The dried oxides have a composition approximating to $Zr_2O_5{\cdot}4H_2O$ and $ZrO_3{\cdot}5H_2O$, though oxygen is lost at 100°, and the product remaining is not definite in composition. Dried at 15°, however, the higher oxide retains the whole of its oxygen, and is evidently more stable than the pentoxide.

Dilute mineral acids and acetic acid, which dissolves freshly precipitated zirconia quite readily, fail to act on these oxides except on prolonged heating.

53. "An Apparatus for the Determination of the Temperature of Decomposition of Salts." By G. H. Bailey, D.Sc., Ph.D.

The apparatus is for the purpose of maintaining a substance at a given temperature for a prolonged period, and permits of the temperature attained being determined, while any change taking place in the substance can be observed. The author proposes to apply it in the first instance to the study of sulphates used in atomic weight determinations. The bulb of an air-thermometer and a narrow tube into which a boat containing the salt to be heated can be introduced are fixed side by side in a hard glass jacket tube, in shape like a test-tube, which can be heated in an iron tube furnace; the capillary stem of the air thermometer is bent at a right angle and its end is connected by a ground joint to the one limb of a **U**-tube, charged with mercury, fixed in front of a graduated scale; the other limb of the tube is arranged to act as a gas regulator. The position of the mercury at various temperatures having been once for all determined, it is easy to observe the temperature within the tube to which the substance is subjected; the temperature can be maintained constant to within a degree or two even at high temperatures; and the

substance may be withdrawn for examination whenever necessary, or products of decomposition may be sucked out from the tube.

54. "The Retention of Lead Salts by Filter-paper." By L. Trant O'Shea.

The absorption effect of filter-paper on dilute solutions of metallic salts has not, so far as the author has been able to ascertain, been studied. His attention was drawn to the subject whilst estimating small quantities of lead in water acidulated with sulphuric acid: although the water was perfectly clear, there was a considerable excess of lead in the unfiltered water over that in the water filtered through a single fluted filter-paper.

To test the generality of the phenomenon, various kinds of filter-paper were used. In all the experiments a solution of lead acetate containing 6 mgrm. lead per litre (0·42 grain per gal.) was used, and in each case 50 c.c. (= 0·3 mgrm. Pb) was passed through the filter-paper folded in the ordinary conical form.

Filter-paper.	Mgrm. Pb in 50 c.c. sol. after filtering through				
	One filter-paper, 7 cm. diam.			Two filter-papers, 7 c.c. diam.	
Schleicher u. Schüll	0·18	0·13	0·15	0·06	0·05
English	0·10	0·09	—	0·03	0·05
French, white	0·11	0·11	—	0·05	0·04
„ grey	0·15	0·17	—	0·06	0·03
German thin (595)	0·17	0·15	—	0·02	0·02
„ thick (597)	0·15	0·10	0·13	0·00	—
„ thickest	0·15	0·13	0·08	0·04	0·06

Though illustrating the phenomenon, these results are not strictly comparable, since the filter-paper was not kept constantly full; consequently larger filter-papers were used which when folded would hold 50 c.c. and the time of filtration was noted.

English Filter-paper.

Time in min.	1·5	1·7	2·25	2·5	2·75	3
Mgrm. Pb in 50 c.c. filtered solution	0·2	0·23	0·17	0·15	0·11	0·08

French, white.

Time in min.	3	4	4·2	7
Mgrm. Pb in 50 c.c. filtered sol.	0·22	0·19	0·09	0·05

French, grey.

Time in min.	3	3	3·5	7
Mgrm. Pb in 50 c.c. filtered sol...	0·14	0·18	0·1	0·07

Washing the filter-paper with water after filtration does not effect the removal of the absorbed salt. A Schleicher and Schüll filter-paper, No. 589, *absorbed* during one filtration of 50 c.c. of solution a quantity of salt equivalent to 0·12 mgrm. lead; it then was washed twice with 50 c.c. water:—

1st washing *contained*..... 0·02 mgrm. Pb.
2nd „ „ ..... 0·00 „

On filtering the same solution twice through the same filter-paper, a quantity of salt equivalent to 0·24 mgrm. Pb was absorbed, and on treating with 50 c.c. water nothing was washed out.

Not only does the absorption take place during filtration, but also when the paper is immersed in the lead solution although at a much slower rate; the amounts of lead remaining after immersing a paper 7 cm. in diameter in 50 c.c. solution (= 0·3 mgrm. Pb) were as follows:—

Time in hours.....	1.	2.	5.	14.
English.....	0·03	0·23	0·23	0·05
French, white	0·25	0·12	0·05	0·00
„ grey.....	0·27	0·17	0·15	0·04
German, thin (595).....	0·25	0·18	0·19	0·03
„ thick (597)	0·25	0·24	0·19	0·00
„ thickest	0·25	0·20	0·18	0·00

ADDITIONS TO THE LIBRARY.

I. *Donations.*

A Manual of Jurisprudence: by A. S. Taylor. Eleventh edition. Edited by T. Stevenson: London, 1886: from the Editor.

A Practical Essay on the Analysis of Minerals: by F. Accum: London, 1804: from R. R. Steele, Esq.

Chemical Amusement, comprising a series of curious and instructive Experiments in Chemistry: by F. Accum: London, 1817: by R. R. Steele, Esq.

Pamphlets:

Experiments on Ensilage, conducted at Rothamsted: Season 1884–5: by J. B. Lawes and J. H. Gilbert: London, 1886.

On the Valuation of Unexhausted Manures: by J. B. Lawes and J. H. Gilbert: London, 1886.

Report of Experiments on the Growth of Wheat for the second period of twenty years in succession on the same ground: by J. B. Lawes and J. H. Gilbert: London, 1885.

On Agricultural Investigation: a Lecture delivered October 27, 1884, at Rutzer's College, New Brunswick, N.J.: by J. H. Gilbert: 1885.

Note on some Conditions of the Development and the Activity of Chlorophyll: by J. H. Gilbert: London, 1885: from the Authors.

The Hell-Gate Explosion near New York, and so-called "Rackarock," with a few words on so-called "Panclastite:" by H. Sprengel: London, 1886: from the Author.

New Experiments on Electricity: by A. Bennet: Derby, 1879. from J. M. Stocks, Esq.

Practical Blowpipe Assaying: by G. Attwood: London, 1880. from the Author.

The Sale of Food and Drugs Acts, 1875 and 1879: with Notes and Cases: by W. J. Bell: London, 1886. from the Author.

Elements of Chemistry in a New Systematic Order: by Lavoisier: translated by R. Kerr: fifth edition: Edinburgh, 1802.

II. *By Purchase.*

Elements of Chemical Physics: by J. P. Cooke, junr.: London, 1886.

Traité élémentaire de Chemie, fondée sur les principes de la Thermochemie: par A. Ditte: Paris, 1884.

RESEARCH FUND.

A meeting of the Research Fund Committee will be held in June. Fellows desiring grants are requested to make application before June 10th.

At the next meeting, on June 3rd, the following papers will be read:—

"The Effect of Remelting on the Properties of Iron. Notes on Sir Wm. Fairbairn's 1853 Experiments." By Thomas Turner.

"Some Ammonium compounds and other derivatives of (α1′) Hydroxyquinoline." By C. A. Kohn, B.Sc., Ph.D.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 25. Session 1885-86.

June 3rd, 1886. Dr. Hugo Müller, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. Bennett F. Davenport, M.A., M.D., 751, Tremont Street, Boston, Mass.; W. Ralph Dodd, 55, Listria Park, Stoke Newington; Albert Brown Lyons, M.A., M.D., Detroit, Michigan, U.S.A.; James B. Readman, F.R.S.E., 9, Moray Place, Edinburgh; Edgar F. Smith, Ph.D., Wittenberg College, Springfield, Ohio.

The following papers were read:—

55. "Notes on Sir W. Fairbairn's Experiments on Remelting Cast Iron." By Thomas Turner, Assoc. R.S.M.

In 1853 Sir W. Fairbairn remelted Eglinton hot-blast pig iron 18 times in order to ascertain the effect produced by repeated melting (B. A. Report, 1853, 87). The metal at first gradually improved, but afterwards rapidly deteriorated, becoming white and hard. The following analyses of the bars are due to Grace Calvert:—

1st melting	Si = 0·77	S = 0·42	C = 2·76
8th „	„ 1·75	„ 0·60	„ 2·30
10th „	„ 1·98	„ 0·26	„ 3·50
18th „	„ 2·22	„ 0·75	„ 3·75

The author recently attempted, with the aid of these results, to explain the effect observed. The accuracy of these analyses had been questioned by Snelus and others, and by the kindness of Professor Unwin the author has been enabled to repeat the chemical examination. His results have been confirmed by separate analyses performed by Mr. J. P. Walton. The mean of their experiments give the following results:—

No. of melting.	Total carbon.	Combined.	Silicon.	Sulphur.	Manganese.	Phosphorus.
1.....	2·67	0·25	4·22	0·03	1·75	0·47
8.....	2·97	0·08	3·21	0·05	0·58	0·53
12.....	2·94	0·85	2·52	0·11	0·33	0·55
14.....	2·98	1·31	2·18	0·13	0·23	0·56
15.....	2·87	1·75	1·95	0·16	0·17	0·58
16.....	2·88	—	1·88	0·20	0·12	0·61

It follows, therefore, that the author's previous conclusions, based upon Calvert's analyses, were erroneous, and that the action of remelting was one of oxidation, resembling in character that of the "refinery," the puddling furnace, the open-hearth furnace, or the Bessemer converter.

56. "Some Ammonium Compounds and other Derivatives of α-1′ Hydroxyquinoline." By C. A. Kohn, B.Sc., Ph.D.

The author first describes the methiodide of hydroxyhydromethylquinoline and its conversion on being heated with solid caustic potash into methoxyhydromethylquinoline: he regards this isomeric change as being due to the formation, in the first place, of potassoxyhydromethylquinoline methiodide, from which potassium iodide is then split off, the added methyl-group taking the place of the displaced potassium. Methoxyhydromethylquinoline methiodide is converted by moist oxide of silver into the corresponding hydroxide, which on heating is decomposed into methyl alcohol and methoxyhydromethylquinoline. The corresponding hydroxyhydroethylquinoline compounds are described. Hydroxyhydroethylquinoline ethiodide yields with caustic potash O. Fischer's ethylkairin; the corresponding hydroxide appears to be decomposed on heating into ethylkairin, ethylene and water. An attempt to prepare a benzyl chloride addition-product of hydroxyhydromethylquinoline was not attended with a satisfactory result: on heating the product with caustic potash what appeared to be a benzylhydromethylquinoline was, however, obtained, and hence it is most probably the added radicle that is displaced.

Acetoxyhydroethylquinoline was also prepared. It possesses only feeble basic properties, and is readily decomposed. By the action of ethylene bromide on hydroxyhydroquinoline a hydroxyhydroethylenequinoline was obtained. Several salts and characteristic reactions of this derivative are described: it is a weak base as well as a weak acid. An investigation of its physiological properties by Professor Filehne shows that it acts like kairin in reducing temperature, but that its

action is a far feebler one—a fact due in all probability to its weaker basic properties. The effect of nitrating ethoxyhydroethylquinoline is also mentioned: two nitro-groups are at once introduced, as is the case with hydroxyquinoline.

57. "β-Sulphophthalic Acid." By Prof. C. Graebe and A. Rée, Ph.D.

The preparation and properties of this acid, in which COOH : COOH : SO_3H = 1 : 2 : 4, and of its salts, are fully described: it may be obtained either by oxidising commercial naphthol yellow S. —dipotassium dinitroalphanaphtholsulphonate—with nitric acid, or by the action of sulphur trioxide on phthalic anhydride, a relatively small amount of the isomeric 1 : 2 : 3 sulphuric acid being also formed in the latter case. The purification of the acid is best effected by means of the monobarium salt, $[C_6H_3(CO_2H)_2 \cdot SO_3]_2Ba \cdot 5OH_2$, one of the most characteristic of its salts. On evaporating an aqueous solution in the water-bath to a syrup, and completing the removal of water by heating in the air-bath below 100°, β-sulphophthalic acid is obtained as a crystalline monohydrate; on heating this at 140°, the acid is obtained as a thick syrup, which may be converted by prolonged heating at 180° into a crystalline mass of anhydrosulphonic acid, $C_6H_3(C_2O_3) \cdot SO_3H$. On treatment with PCl_5, sulphophthalic acid yields two acid chlorides—a crystalline monochloride, $C_6H_3(COOH)_2 \cdot SO_2Cl$, from which the corresponding sulphonamide may be obtained by the action of ammonia, and a non-crystalline trichloride, $C_6H_3(C_2O_2Cl_2) \cdot SO_2Cl$, which decomposes on distillation into SO_2 and β-chlorophthalic chloride.

58. "Compounds obtained by the aid of β-Sulphophthalic Acid." By the same.

β-Hydroxyphthalic acid was obtained by fusing sodium β-sulphophthalate with $2\frac{1}{2}$ times its weight of sodium hydroxide at a temperature not exceeding 180°; if this temperature be much exceeded, methydroxybenzoic acid is produced, this acid being also formed in theoretical quantity on heating β-hydroxyphthalic acid with dilute muriatic acid at 180°.

β-Hydroxyphthalimide was prepared by acting with ammonia on β-hydroxyphthalic anhydride; it is converted into *β-hydroxyphthalide* by digestion with tin and muriatic acid, and treatment of the nitroso-derivative of the β-hydroxyphthalidine thus formed with caustic soda.

By heating the monochloride of β-sulphophthalic acid with phosphorus pentachloride at 220°, a quantitative yield of *β-chlorophthalic chloride*, and consequently of β-chlorophthalic acid, may be obtained.

The chloride boils at 275°; *β-chlorophthalic anhydride* melts at 99° and boils at 296° (corr.). The same methylic salt is obtained by the action of methylic alcohol on β-chlorophthalic chloride and anhydride, and by the action of methyl iodide on silver β-chlorophthalate: this result is of interest, as on the assumption that phthalic chloride is of unsymmetrical constitution ethereal salts prepared from a phthalic chloride should differ from those obtained either from the anhydride or the silver salt, and this has been proved to be true in the case of tetrachlorophthalic acid.

β-Chlorophthalimide, obtained by the action of ammonia on the anhydride, melts at 210—211°. *β-Chlorofluoresceïn* closely resembles fluoresceïn.

By the action of aluminium chloride on a benzene solution of β-chlorophthalic anhydride, *metachlorobenzoylbenzoic acid* is formed, from which *metachloranthraquinone* is readily obtained by condensation with sulphonic acid.

On fusion with sodic formate, β-sulphophthalic acid yields trimellitic (1 : 2 : 4 benzenetricarboxylic) acid.

59. "Derivatives of Taurine." Part II. By J. William James.

An account is given of experiments to determine the constitution of the trimethyltaurine previously described by the author (Trans., 1885, 367). Boiling iodhydric acid has no action on it: therefore as all compounds containing methoxyl yield methyliodide when thus heated, the formula $NMe_2 \cdot C_2H_4 \cdot SO_2OMe$ is excluded. Trimethyltaurine is readily decomposed by boiling with alkalis, trimethylamine and isethionate being formed; cyanamide does not combine with it: hence it must be supposed that it differs in constitution both from taurine and the mono- and dialkyl-taurines—which are not decomposed by alkalis but all form crystalline compounds with cyanamide. The author therefore represents the trialkyltaurines alone as analogues of betaine, thus :—

$$C_2H_4\begin{cases}NH_2\\SO_2\cdot OH\end{cases} \qquad C_2H_4\begin{cases}NHR'\\SO_2\cdot OH\end{cases} \qquad C_2H_4\begin{cases}NR_2'\\SO_2\cdot OH\end{cases} \qquad C_2H_4\begin{cases}NR_3'\\ \diagdown\\SO_2\cdot O\end{cases}$$

Taurine. Monalkyltaurine. Dialkyltaurine. Trialkyltaurine.

Finally, a description is given of an *imide* of the formula

$$C_2H_4\left\{\begin{matrix}NH\\SO_2\end{matrix}\right\},$$

obtained by the action of dry ammonia-gas on an ethereal solution of β-chlorethanesulphonic chloride, $Cl \cdot C_2H_4 \cdot SO_2Cl$; it is an extremely stable body, not being decomposed by boiling with alkalis; the imidic hydrogen can be displaced by metals.

Discussion.

Dr. Armstrong expressed the opinion that the properties of taurine and its derivatives were such that it was impossible to represent them as sulphonic *acids;* he thought that they were all equally to be regarded as ammonium compounds of the glycine and betaine type, and judging from their physical properties that neutralisation was probably brought about by the union of 2 mols. of the parent amido-sulphonic acid. The evidence brought forward was scarcely sufficient to warrant the assumption that trimethyltaurine was essentially different in constitution from taurine and the mono- and di-alkyl-taurines.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Watts's Manual of Chemistry, Theoretical and Practical, based on Fownes's Manual. Vol. II. Chemistry of Carbon Compounds, or Organic Chemistry. Second edition (13th ed. of Fownes): by W. A. Tilden. London, 1886. from the Author.

Department of Agriculture (U.S.). Division of Chemistry Bulletin. No. 8. Methods and Machinery for the Application of Diffusion to the Extraction of Sugar from Sugar-cane and Sorghum: by H. W. Wiley. No. 10. Principles and Methods of Soil Analysis: by E. Richards. No. 11. Second Report of Experiments in the Manufacture of Sugar at Magnolia Station, Lawrence, La.: by G. I. Spencer Washington, 1886. from the Department.

II. *By Purchase.*

Analyse der Fette und Wachsarten: von R. Benedikt. Berlin, 1886.

Wöhler's Grundriss der organischen Chemie: von R. Fittig. 11te Aufl., 1ste Hälfte. Leipzig, 1885.

Die Chemie des Steinkoplentheers, mit besonderer Berücksichtigung der künstlichen organischen Farbstoffe: von G. Schultz. Erster Band: die Rohmaterialien: erste Lieferung. Braunschweig, 1886.

Étude pratique sur le Ciment Portland: par E. Candlot. Paris, 1886.

Index der Krystallformen der Mineralien: von V. Goldschmidt. Erste Lieferung. Berlin, 1886.

Dr. Sprengel desires it to be mentioned that at the meeting on May 20th he also exhibited three photographs taken at the moment of the explosion at Hell Gate, October 10th, 1885, when the mine was

charged with 22 tons dynamite and 107 tons of a mixture of 21 parts nitrobenzene and 79 parts potassium chlorate. This mixture belongs to the safety explosives described by Dr. Sprengel in the *Chem. Soc. J.*, 1873, and according to General Abbot, U.S. Army, has the power 109, dynamite with 75 per cent. nitroglycerine being 100.

Erratum.—In the formula at bottom of p. 204, insert an S between the two P's.

At the next meeting on June 17th, there will be a ballot for the election of Fellows, and the following papers will be read:—

1. "The Electrolysis of Aqueous Solutions of Sulphuric Acid." By Prof. H. McLeod, F.R.S.
2. "Essential Oils (Part III), their Refractive and Dispersive Power." By Dr. J. H. Gladstone, F.R.S.
3. "The Formation and Destruction of Nitrates and Nitrites in Artificial Solutions and in River and Well Waters." By J. M. H. Munro, D.Sc.
4. "An Apparatus for Distillation under Reduced Pressure." By Dr. W. H. Perkin, F.R.S.
5. "The Electromotive Force produced by the Combination of Cadmium and Iodine in Presence of Water." By A. P. Laurie.
6. "A Method of Investigating the Constitution of Azo-, Diazo-, and Analogous Compounds." By R. Meldola, F.R.S., and F. W. Streatfeild.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 26. Session 1885-86.

June 17th, 1886. Dr. Hugo Müller, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. Alfred Rée, Apperley Bridge, near Leeds; Vivian Phelps Richards, 28, Boscombe Road, Shepherd's Bush, W.; Laurence Hislop, Saltney, Chester; Frank Thomas Shutt, B.Sc., Rosedale Cottage, Toronto, Canada.

The following were duly elected Fellows of the Society:— Thomas Akitt; James Blake, M.D.; Alfred Chaston; A. W. H. Chapman; Augusto Cæsar Diojo; Charles A. R. Jowitt; Charles Alexander Kohn; John Temple Leow; William Ray; Joseph Price Remington; William Richards; Forbes Rickard; William Saunders; Charles A. Smith.

The following papers were read:—

60. "The Electrolysis of aqueous solutions of Sulphuric Acid, with special reference to the forms of Oxygen obtained." By Professor H. McLeod, F.R.S.

The experiments were instituted to determine the quantity of ozone that can be obtained by electrolysis. The negative electrode consisted of a small platinum plate, and the positive of a tube containing mercury and with fine platinum wires of 0·045 mm. and 0·027 mm. in diameter fused into the glass. Several wires were used, the total length being about 6 mm. The electrolysis was carried out in a U-tube surrounded by ice and water; the hydrogen was collected over water, and the ozonised oxygen passed through a tube containing a solution of potassic iodide, the oxygen being afterwards collected. The quantity of ozone was determined by acidifying the

potassic iodide solution and decolorising by a standard solution of sodic thiosulphate. In the electrolysed acid an oxidising substance is present which is not hydroxyl, but is probably Berthelot's persulphuric acid. The amount of this "active oxygen" was found by adding potassic iodide to the liquid and decolorising by the solution of thiosulphate. The electric current was measured by a tangent galvanometer, and the dimensions of the wires of the positive pole were determined; from these data the intensity of the current was calculated. Acids were used of relative densities varying between 1·025 and 1·7. The maximum quantity of ozone was obtained with solutions about 1·075 or 1·1 in density, the electrolytic oxygen containing about 16 or 17 per cent. of its weight of ozone. The maximum quantity of "active oxygen" in the oxidising substance referred to was produced with acids about 1·2 to 1·25 in density, the proportion being 16 or 17 atoms to 100 atoms of hydrogen.

The solubility of ozone was determined by one experiment and found to be much greater than that of oxygen.

A note is added to the paper detailing some experiments on the action of oxygen on chlorhydric acid under the influence of light: it was found that a considerable quantity of chlorine was liberated.

Discussion.

Mr. Friswell said that Professor McLeod's observation explained a fact that had come under his notice years ago; viz., the constant presence of chlorine in muriatic acid.

The President said that he also had noticed this, and had found that chlorine was always contained in the acid if it had been exposed to the air.

Mr. Laurie suggested trying aluminium electrodes; he had noticed a very distinct smell of ozone on electrolysing dilute sulphuric acid with poles of this metal.

61. "Essential Oils (Part III): their Specific Refractive and Dispersive Power." By Dr. J. H. Gladstone, F.R.S.

Since the appearance of the author's former papers on essential oils in 1863 and 1872, many investigations have been published; but important divergences of opinion still exist among chemists as to the rational constitution of these compounds. He now brings forward arguments founded on the phenomena of refraction and dispersion, believing that in the conflict of opinions such arguments ought to have considerable force. For this purpose he employs the refraction equivalent for the solar line A, as compared with that calculated from the known values of carbon and hydrogen and the known increase on

account of the double linking of carbon-atoms. But he also introduces a new conception, that of dispersion equivalents: being the difference between the refraction equivalents for the lines A and H, or $P\frac{\mu_H - \mu_A}{d}$, where μ and d are the refractive index and relative density and P the atomic weight. It is found that the dispersion equivalent of carbon may be taken at 0·25, and that of hydrogen at 0·045, as a first approximation, while in the case of benzenoid compounds the addition to be made to the dispersion equivalent on account of each double linking of carbon-atoms is fully 0·8.

The paper deals mainly with the $C_{10}H_{16}$ hydrocarbons. These are divisible on account of their physical and chemical properties into two large groups, the terpenes and the citrenes. There are also the solid camphenes and the cedrenes or C H_{24} hydrocarbons. The optical properties of the terpenes are in close accordance with what may be expected from a compound in which one pair of carbon-atoms is double-linked; those of the citrenes indicate two pairs; while camphene has a slightly slower specific refraction and dispersion, however, than a terpene. The cedrenes appear to be strictly polymeric with the terpenes from an optical point of view.

The optical properties of caoutchone were also examined. Its principal constituent resembles the citrenes; so also does the liquid hydrocarbon, $C_{10}H_{16}$, that is produced by its dry distillation. Isoprene, C_5H_8, also, must have two pairs of its carbon-atoms double-linked, a result which agrees with Tilden's conclusions from its chemical properties.

	Refraction equivalent.		Dispersion equivalent.	
	Observed.	Calculated.	Observed.	Calculated.
Terpenes, natural	73·0	73·0	4·0	4·02
„ artificial.....	72·9	73·0	3·9	4·02
Camphene.....	71·9	73·0	3·7	4·02
Cedrenes	109·8	109·5	6·1	6·03
Citrenes, natural	75·0	75·2	4·5	4·82
„ artificial	75·1	75·2	4·6	4·82
Caoutchene.....	75·3	75·2	5·0	4·82
Isoprene	40·3	39·8	3·2	3·21

Armstrong's cymhydrene, $C_{10}H_{20}$, Atkinson's menthene, $C_{10}H_{18}$, citrene, $C_{10}H_{16}$, and cymene, $C_{10}H_{14}$, form a series: the first being a saturated compound, and the others having respectively one, two and three pairs of carbon-atoms double-linked.

Discussion.

Prof. Tilden asked whether Dr. Gladstone had made any special attempt to determine the composition of the cedrenes; they were commonly regarded as $C_{15}H_{24}$ hydrocarbons, but the difference in composition between $C_{15}H_{24}$ and $C_{15}H_{26}$ was so slight that it was conceivable that the cedrenes were in reality homologues of the terpenes.

Dr. Gladstone said that this suggestion was novel to him.

Dr. Armstrong thought that while Dr. Gladstone's observations agreed with the chemical evidence in assigning the terpenes to a position intermediate between the camphenes and citrenes, the chemical evidence did not harmonise with the assumption that the terpenes contained only a single pair of "double linked" carbon-atoms; in this respect the terpenes and citrenes must be classed together. In point of fact the $C_{10}H_{16}$ hydrocarbons manifest peculiarities which at present do not admit of satisfactory representation by a symbolic expression.

62. "The Formation and Destruction of Nitrates and Nitrites in Artificial Solutions and in River and Well Waters." By J. M. H Munro, D.Sc.

Most of the experiments recorded in this paper were made in the years 1883 and 1884, the method followed being that adopted by R. Warington and described in his Second Report on Nitrification (1879).

Many of the general conditions of nitrification, as stated by Schloesing and Muntz, and by Warington, have been confirmed. For example, in no case has nitrification occurred in a solution sterilised by boiling after being seeded with soil and left unopened until tested after an interval of as much as three years. Mercuric chloride, lead acetate and chloroform are all equally fatal to nitrification. As an instance of the slowness of the process in some cases, a solution of 2 grams per litre of ammonium chloride seeded with 2 grams of soil commenced nitrifying only after an incubation of three months, and required two years and ten months for complete nitrification; but when a fresh solution of 1 gram per litre of ammonium chloride was added bodily to this nitrified solution, it commenced to nitrify after an incubation of only five days.

Amongst nitrogenous bodies other than ammonium salts, *ethylamine hydrochloride*, *gelatin*, *potassium* and *ammonium thiocyanate* and *urea* are all easily susceptible of complete nitrification in contact with soil. In all these cases ammonia is first formed, and nitrite appears at a subsequent stage, finally passing into nitrate. Thiourea has resisted repeated attempts to nitrify it.

Several experiments are cited to show that the organic carbon

required in a solution prepared for nitrification is infinitesimal in proportion to the quantity of ammonium salt nitrified. Thus 63 mgrms. ammonium chloride have been completely nitrified to nitrite without any added organic carbon. When an alkaline tartrate or any similar organic matter is included in a solution prepared for nitrification (as has been the case in all published experiments), it delays nitrification, and even brings about a destruction of any nitrate that may pre-exist in the solution *unless all other germs than those of the nitrifying organism are rigorously included.* It does this because it encourages a growth of *denitrifying bacteria*, the germs of which exist in the air, in soil, in natural waters and generally even in the few drops of nitrifying solution employed as seed. Until these bacteria have run their course and died, nitrification does not commence, and hence there is a period of apparent incubation even in solutions otherwise ready for immediate nitrification. By using soil as seed and excluding all other added organic matter, a first solution of ammonium chloride may be caused to commence nitrifying in three or four days; if after nitrification this is poured off and replaced by a second solution, nitrification commences in 24 hours; and a third solution employed in a similar manner may (under favourable circumstances) be seen to have commenced nitrifying in seven hours.

Well and river waters, since they contain organic matter not fermentible by denitrifying bacteria, form suitable media for the study of nitrification. The salifiable base (calcium carbonate) and the traces of necessary minerals are also present in suitable proportions and in such a form as not to interfere with the perfect transparency of the solutions. Such waters, boiled and filtered and seeded with a little soil, or a few drops of a nitrifying solution, will nitrify added ammonium chloride to the full saturating capacity of the calcium carbonate contained in them. The process usually takes 30—40 days at the ordinary temperature.

The question as to how far these natural waters contain the nitrifying organism independently of added soil has also been carefully tested. A suitable quantity of ammonium chloride solution (5 c.c. = 5 mgrm. NH_3) is boiled in a sterilised flask plugged with cotton-wool; on cooling, the plug is removed for a moment while the flask is half filled with the water to be examined. A cap of paper is then tied over the flask, which is placed in a warm place (not over 85°F.) for 18—30 days and then opened and tested. If the water possess any nitrifying power some nitrite will almost certainly be found at the end of this period by the metaphenylenediamine test. Eleven waters tested in this way were found to possess nitrifying powers in different degrees: they included river-water, seven well-waters, water from a coal-pit level, rain-water from a brick cistern and water from the

Bristol Waterworks Company's main. The wells with sewage contamination, present and past, nitrified readily: probably because the nitrifying organism has already undergone a period of incubation and is in full activity. River water commences nitrifying after 9 days, and finishes on the 46th day, nitrite being present as late as the 42nd day. The addition of 1 per cent. of soil hastens the process and lessens the production of nitrite. The only water which failed to produce nitrification after an incubation of 18 days at 80—85°F. was rain-water caught from the clouds in a sterilised beaker and added to boiled well-water. Well-water will produce a purely nitrous or a purely nitric fermentation, according to circumstances, and the nitrite may persist for at least two years without further oxidation. The nitrifying power of a well-water is not removed by filtration through Swedish paper, and is even increased by filtration through a charcoal filter in common use. The waters remain practically clear throughout, and the deposit is extremely slight; as they encourage the growth of the nitrifying organism almost exclusively (in the dark) they are probably well suited for microscopic observation of this organism.

Denitrification.—An alkaline tartrate, acetate, or oxalate, sugar, glycerol, or in fact *any* fermentible organic matter, if added to well-water, produces a bacterial reduction or destruction of the nitrate pre-existing in the water. The tartrate, acetate, or oxalate is destroyed with formation of an alkaline carbonate. The water becomes opalescent in 3—4 days, and consistently with this a trace of nitrite is found. In a few more days all the nitrate may be reduced to nitrite. In good waters the reduction may go no further. In many polluted waters, the nitrate and nitrite are totally destroyed, nitrogen gas being evolved. The same effect is produced by the addition of a few drops of sewage to the water, *if the water contain any fermentible organic matter.* Even salicylic acid and phenol lend themselves to this reduction, although they are fatal to nitrification. MM. Gayon and Dupetit, in a memoir published since this paper was in MSS., have examined this phenomenon in great detail by the culture of the denitrifying bacteria in highly artificial solutions. The bacteria which effect the reduction to nitrite in presence of organic matter are common in the air, waters and soil. Those which destroy the nitrate or nitrite with evolution of nitrogen gas were obtained by MM. Gayon and Dupetit from sewage.

63. "Water of Crystallisation." By W. W. J. Nicol, M.A., D.Sc., F.R.S.E.

The paper is a reply to Professor Pickering's criticism of the

author's experiment on the molecular volumes of salts in solution. (Trans., 1886, 411—432.) The author maintains the accuracy of his experiments and of the conclusions derived from them, which are that when a salt is dissolved water of crystallisation is indistinguishable from solvent water, both having the same volume; and that water of constitution has in solution a volume markedly different from that of solvent water. Hence it seems certain that water of crystallisation does *not* exist in solution, but that the whole of the water present is in the same relation to the salt, no hydrate definite or indefinite existing in solution. This is supported by experiments on supersaturation, the author having prepared supersaturated solutions from dehydrated salt and *cold* water: the salt dissolving with evolution of heat but without the formation of a hydrate.

Discussion.

Mr. Pickering said that he did not wish for one moment to call in question Dr. Nicol's results, and he even agreed with him so far as to admit that the work showed no difference between combined water and water of solution; but this was a very different thing to saying that it proved that no water was combined with the salt. He had ample reason for considering that this was a case in which negative evidence proved nothing.

He considered that Dr. Nicol's experiments on the magnesium sulphates afforded the strongest evidence which we have of one of the water molecules contained in them being different from the rest. At the same time he thought that that evidence was far too slight to warrant any positive conclusion being drawn; and even if it proved that such a difference did exist, it would not prove that this one molecule was so-called constitutional water. A discussion of the thermal phenomena attending dissolution would open the whole question of the nature of solution, into which it was impossible then to enter. Although Mr. Pickering could not accept Dr. Nicol's theory of solution, he by no means adhered to what is ordinarily understood by the "hydrate theory." It was impossible he thought to draw any general conclusions as to the nature of solution from the behaviour of one of the most exceptional salts which we know, sodium sulphate.

Dr. Nicol said that he was glad to hear that Mr. Pickering had no wish to call in question the accuracy of his results, for that was not the impression to be gathered from Mr. Pickering's paper. As to negative evidence proving nothing, he thought that it should have at least as much weight as an affirmative statement, unsupported by any evidence other perhaps than the colour of cobalt and copper chlorides. In using the term constitutional water, he had no intention of com-

mitting himself to more than the statement that one water molecule was differently related to the salt in solution from the remainder of the water. With regard to the dissolution of a dehydrated salt without the intermediate formation of a hydrate, he had used sodium sulphate as the most convenient, but had performed similar experiments with sodium thiosulphate, magnesium sulphate and other salts. He was of the opinion that such experiments are conclusive evidence against the existence in solution of hydrates of these salts.

Dr. Armstrong called attention to T. Thomsen's recent observations on the supposed division of the water between two bodies in solution (*J. pr. Chem.*, 1885, **32**, 211; *Chem. Soc. Abs.*, 1886, 12).

64. "A Method of investigating the constitution of Azo-, Diazo- and analogous Compounds." By R. Meldola, F.R.S., and F. W. Streatfeild.

The method described consists in displacing the hydrogen in such compounds by alkyl radicles and then decomposing by heating with acids or by complete reduction. The compound described in the present paper is paradinitrodiazoamidobenzene obtained by treating paranitraniline dissolved in chlorhydric acid with the necessary quantity of sodium nitrite. The formula of this substance is that of a true diazoamidoazo-compound, viz., $NO_2 \cdot C_6H_4 \cdot N_2 \cdot NH \cdot C_6H_4 \cdot NO_2$. On reduction by tin and hydrochloric acid it gives only paraphenylenediamine. It is a strongly acid substance, the H of the $\cdot N_2.NH\cdot$ group being displaceable by metals with the formation of crystalline salts. It is remarkably stable in the presence of alkalis, but is decomposed on heating with acids. Its differs from other diazoamidocompounds, however, in not furnishing a phenol as a product of decomposition by acids. With dilute sulphuric acid it gives paranitraniline and a tarry substance, and with chlorhydric acid, paranitraniline and paranitrochlorbenzene :—

$$NO_2 \cdot C_6H_4 \cdot N_2 \cdot NH \cdot C_6H_4 \cdot NO_2 + HCl = N_2 + NO_2 \cdot C_6H_4Cl + NO_2 \cdot C_6H_4 \cdot NH_2.$$

By acting with ethyl iodide upon the sodium salt the ethyl-derivative, $NO_2 \cdot C_6H_4 \cdot N_2 \cdot N(C_2H_5)C_6H_4 \cdot NO_2$, is obtained. The original substance forms small yellow needles, melting with decomposition at 223°. The ethyl-derivative melts at 191—192°. The last compound does not form salts; it is decomposed by dilute sulphuric acid into ethyl paranitraniline and resinous products, and by chlorhydric acid into paranitrochlorobenzene and ethylparanitraniline. The ethylparanitraniline forms a nitroso-derivative (m. p. 119·5°), which is described in the paper. The authors point out that the decomposition of the

ethyl-derivative into ethylnitraniline and nitrochlorbenzene is conclusive evidence against the symmetrical formulæ—

$$NO_2{\cdot}C_6H_4{\cdot}N{-}N{\cdot}C_6H_4{\cdot}NO_2\,;\quad NO_2{\cdot}C_6H_4{\cdot}N{-}N{\cdot}C_6H_4{\cdot}NO_2,$$
$$\diagdown\!\diagup \qquad\qquad\qquad\qquad\qquad\qquad \diagdown\!\diagup$$
$$NH \qquad\qquad\qquad\qquad\qquad\qquad N(C_2H_5)$$

for this compound and the original substance. They propose to extend the investigation to other diazo-, azo- and oxyazo-compounds.

65. "The Estimation of free Oxygen in Water." By Miss K. I. Williams and Professor W. Ramsay.

The authors have instituted a comparison of Schützenberger's methods of estimating free oxygen in water with each other and with the gasometric method with favourable results. Schützenberger's first method, which consists in adding sodium hyposulphite to a measured quantity of water, using indigo-carmine as an indicator, is stated by him to estimate only half the amount of free oxygen; his second method in which water containing free oxygen is added to indigo-white, turning it blue, and the amount of oxidised indigo-white is estimated by hyposulphite, was regarded by him as the only accurate one. The authors disprove the assertion, and show that there is a preliminary stage in the first process when colour disappears; but that on standing for some time a blue colour appears, to destroy which permanently requires such an addition of hyposulphite as to make the total amount equal to that employed in operating according to the second method. The proportion of hyposulphite used during the first stage of Method I to the total amount used is 3 to 5; but they believe that this proportion was conditioned by the temperature and dilution prevailing during the experiments. It is also shown that hyposulphite of soda reacts to some extent with hydrogen dioxide, thus negativing the statements of Schützenberger's of König.

66. "Note as to the Existence of an allotropic modification of Nitrogen." By Miss K. I. Williams and Professor Ramsay.

Attention was some time ago directed to the existence of an allotropic modification of nitrogen by Mr. J. Stillingfleet Johnson, who stated that an active modification of this element could be prepared by heating a mixture of potassium nitrite and ammonium chloride solutions; and that on passing the evolved gas over heated platinum sponge along with hydrogen, ammonia was formed. The support lately given to this statement by the experiments of Professors J. J. Thomson and

Threlfall has suggested the propriety of testing Johnson's statements by further experiments; the results, however, have been negative. The hydrogen used in the experiments was prepared by the action of chlorhydric acid on granulated zinc. It was collected in a gasholder and dried by passing it first through sulphuric acid and then over phosphoric anhydride. In preparing the nitrogen, 85 grams of potassium nitrite was dissolved in distilled water and added to a solution of 53·4 grams of ammonium chloride; some ammonia and then some crystals of cupric chloride were introduced. On the addition of a sufficient proportion of this latter compound a steady stream of gas came off and was collected in a gasholder. In order to dry it and remove any oxides of nitrogen or ammonia present in the gas, it was first passed through a tube containing pumice-stone soaked in an acid solution of ferrous sulphate, next through a wash-bottle partly filled with sulphuric acid, over pumice-stone soaked with Nessler's reagent, then over pumice-stone soaked with sulphuric acid, and then through a tube filled with phosphoric anhydride. At this point the two streams of gas were brought together by a T-tube, and the mixture passed over heated platinum sponge into bulbs containing chlorhydric acid. At the end of each experiment the contents of the bulbs was washed into an evaporating basin and evaporated over a water-bath; the residue was then dissolved in distilled water and tested for ammonia with Nessler's reagent.

The first experiment was made with about 4·38 litres of nitrogen prepared at a temperature of about 100°; the result being that the Nessler's reagent was coloured merely a faint yellow. In a second experiment, the nitrogen used was evolved at first from the mixed solution by external application of heat, but on adding more cupric chloride the reaction went on alone and the temperature was lower than in the first experiment. To get accurate results the capacity of the nitrogen gasholder was gauged; when full of water it contained 8·481 litres, equal to 7·7031 litres at 0° C. and 760 mm. After using the whole of this nitrogen, at the end of the experiment the same tint was obtained as that given by 1·10 c.c. of ammonium chloride solution in 100 c.c. of distilled water with Nessler's reagent, 1 c.c. of the ammonium chloride containing 0·00019107 gram NH_4Cl or 0·00005 gram N. Therefore the amount of "active nitrogen" was only 0·000055 gram in the 7·7031 litres.

To obtain better results, if possible, during the preparation of the next gasholder full of nitrogen, the flask from which it was evolved was carefully kept below 50° C., the temperature being watched by means of a thermometer placed in the cork of the flask. In this case the ammonia formed produced the same tint with Nessler's reagent as that given by 1·14 c.c. of the standard ammonium chloride solution,

proving the presence of only 0·000057 gram "active nitrogen" in 7·7031 litres. It is evident, therefore, that these experiments fail to corroborate Mr. Johnson's results.

67. "The Presence of a reducing agent, probably Hydrogen Peroxide, in Natural Water." By Professor Ramsay.

Distilled water, as well as ordinary tap water, has a reducing action on potassium permanganate. The amount of the reducing agent is increased by evaporation, even when all possibility of contamination with solid organic impurity is excluded. The amount of reduction is far too great to be ascribed to the nitrites present in the water. The experiments described in the paper show under what circumstances and to what extent this substance—which is probably hydrogen dioxide—is produced. If this supposition be correct and the active substance in natural water be really hydrogen peroxide, it becomes of importance to ascertain its action on organic impurities contained in many natural waters. Experiments were therefore made quantitatively on the action of dilute solutions of peroxide of hydrogen on urea, and it was found that the urea is slowly oxidised on standing; the rate of this action has also been measured. (Comp. H. B. Dixon, *Chem. Soc. Trans.*, 1886, p. 108.)

68. "Evaporation and Dissociation. Part IV. A Study of the thermal properties of Acetic Acid." By W. Ramsay, Ph.D., and Sydney Young, D.Sc.

This paper contains a record of measurements of the relative density of liquid acetic acid at 13·11° (water at 4° = 1·0), the number obtained being 1·05682; its expansion up to a temperature of 280°, at which the volume of 1 gram is 1·5172 c.c.; its vapour-pressures, which reach 24600 mm. at 280°; and the density of its saturated and unsaturated vapour at different temperatures and pressures. The minimum value of the density of the saturated vapour is at 150°, and is equal to 50·06 (H = 1·0); it increases both with rise and with fall of temperature. The values of $\frac{dp}{dt}$ have also been calculated, and from them and from the other data the heats of vaporisation have been deduced. Here, again, there is a maximum value at 110·6°; the latent heat at this point is 92·8 C., and decreases both with rise and fall of temperature. Diagrams are appended contrasting the behaviour of acetic acid with that of alcohol and of ether.

69. "Note on the Vapour-densities of Chloral Ethyl-Alcoholate." By William Ramsay, Ph.D., and Sydney Young, D.Sc.

This paper contains an account of determinations of the densities

of the saturated and unsaturated vapour of chloral ethyl-alcoholate. The amount of dissociation is always very great, the percentage number of molecules decomposed being never less than 75. Owing to the very small variation of vapour-density under different conditions of pressure and temperature, to the impossibility of obtaining very concordant results with such a substance, and to the fact, noticed to a smaller extent with acetic acid, that on decreasing the volume condensation begins before the pressure has reached its maximum, it is impossible to draw any very definite conclusion regarding the relation of the density of the saturated vapour of this body to the temperature, but it may be stated that a rise in the density of the saturated vapour with fall of temperature could not be detected. The density of the unsaturated vapour diminishes with rise of temperature at constant pressure, and with fall of pressure at constant temperature.

70. "The Nature of Liquids as shown by a study of the thermal properties of stable and of dissociable Bodies." By William Ramsay, Ph.D., and Sydney Young, D.Sc.

After Deville advanced the theory of dissociation, its opponents endeavoured to explain the abnormality of the vapour-density of unstable bodies by ascribing it to a deviation from Avogadro's law supposed to occur in many liquids at temperatures and pressures near their condensation points. No complete research having been made to compare the behaviour of stable and of dissociable bodies in this respect, the authors have investigated the thermal properties of alcohol, ether, acetic acid and chloral alcoholate. In all cases, they have found abnormality at high pressures. But whereas with alcohol and with ether the density of the saturated vapour becomes and remains normal below certain temperatures, with acetic acid the density when at its lowest is abnormally high and increases with fall as well as with rise of temperature. The two theories alluded to above, by which attempts have been made to explain this abnormal density, are (1) that the gaseous molecules exercising attraction on one another are thereby drawn closer together, and (2) that gaseous molecules combine to form more complex molecules such as are by many supposed to exist in liquids. It appears to the authors inconceivable that this effect should be produced by the same cause under conditions so totally different: for at low temperatures the stability of a saturated vapour is greater while the molecules are necessarily further apart; and at high temperatures, owing to the high pressure, the molecules are in closer proximity, while the stability is necessarily decreased. With acetic acid, it appears therefore that the abnor-

mality at high temperatures is due to a physical cause, common to all liquids, but at low temperatures must be ascribed to some sort of chemical combination between the gaseous molecules.

71. "The Electromotive Forces developed during the combination of Cadmium and Iodine in Presence of Water." By A. P. Laurie, B.A., B.Sc.

The author has determined by means of a Thomson electrometer the electromotive forces of cells consisting of a cadmium and a platinum plate immersed in a solution of cadmium iodide containing free iodine. In one set of experiments, the amount of cadmium iodide in solution was constant and the amount of iodine was varied; in another the amount of cadmium iodide varied, the solution being in each case saturated with iodine; in a third, a constant amount of iodine, but varying amounts of cadmium iodide were used. The result of the experiments is to show that if cadmium and water containing cadmium iodide and free iodine are brought together, a considerable electromotive force is developed, which steadily falls. This depends on the facts (1) that as the free iodine is diminished, the electromotive force falls gradually at first, but more rapidly the less iodine there is present; (2) that as the cadmium iodide solution increases in strength, the electromotive force falls off very rapidly while very small quantities of the salt are present but more and more slowly as the amount of salt present becomes considerable. In both cases the change may be represented by a continuous curve. The actual values are given in the paper.

72. "Detection and Estimation of Iodine, Bromine and Chlorine." By M. Dechan.

To separate iodine from a mixture of chloride, bromide and iodide, the author distils with a concentrated solution of potassium bichromate (40 grams $K_2Cr_2O_7$ to 100 c.c. water); on repeating the distillation, after adding a small quantity of sulphuric acid, the bromine only passes over, provided that the solution be not too concentrated. The apparatus is therefore so arranged that by means of a stopcock funnel water may be added whenever necessary. The following results are quoted :—

Iodine.		Bromine.		Chlorine.	
Taken.	Found.	Taken.	Found.	Taken.	Found.
0·01443	0·01441	0·0126	0·01254	0·0123	0·0122
0·0288	0·02833	0·0252	0·0250	0·056	—
0·0576	0·05628	0·0504	0·05009	0·194	—

73. "The Analysis of Alloys and Minerals containing the heavy Metals, Selenium, Tellurium, &c." By Thomas Bayley.

The metals precipitable as sulphides are commonly divided into the two groups of those forming sulphides insoluble in alkaline sulphides, and those whose sulphides are soluble; the method of extraction with an alkaline sulphide is often applied in qualitative but less often in quantitative analysis, owing to the difficulty of completely removing the soluble sulphides when once they have been precipitated in admixture with the other sulphides. Instead of precipitating both classes together, it is better, the author finds, to prevent the precipitation of the thio-salt forming elements altogether, experience having shown that the process conducted on this principle is at once accurate and very easy of execution. The process recommended consists in passing sulphuretted hydrogen into a boiling solution containing the substance together with citric and tartaric acids and caustic soda.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Select Methods in Chemical Analysis (chiefly Inorganic): by W. Crookes: second edition, re-written and greatly enlarged: London, 1886: from the Author.

Notes on Analytical Chemistry for Students in Medicine: by A. J. Bernays: second edition: London, 1886: from the Author.

New Commercial Plants and Drugs: by T. Christy: No. 9: London, 1886:

II. *By Purchase.*

Electro-deposition: a Practical Treatise on the Electrolysis of Gold, Silver, Copper, Nickel, and other Metals and Alloys; with several chapters on Electro-metallurgy: by A. Watt: London, 1886.

Spectrum Analysis in its Applications to Terrestrial Substances and Physical Constitution of the Heavenly Bodies, familiarly explained by the late Dr. H. Schellen: translated from the third enlarged and revised German edition by Jane and Caroline Lassell, edited with notes by W. de W. Abney: London, 1885.

Die Chemie des Steinkohlentheers: von G. Schultz: Zweite Auflage, Zweite Lieferung: Braunschweig, 1886.

HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY, ST. MARTIN'S LANE.

ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 27. Session 1885–86.

Titles of papers received and printed in the Transactions during the recess.

74. "Phenylsulphonic Anhydride." By J. L. H. Abrahall.

75. "The Action of Hexabromacetone on Urea." By Alfred Senier.

76. "Contributions to our Knowledge of the Chlorides of Antimony." By Richard Anschütz and P. Norman Evans.

77. "Pipitzahoic Acid." (First Communication.) By Richard Anschütz and John Walter Leather.

78. "Further Contributions to the Knowledge of Cyanuric Chloride and other Cyanuric Derivatives." By Harold H. Fries.

79. "Further Observations on the Action of Hexabromacetone on Urea." By Alfred Senier.

80. "The Constitution of Diazobenzeneanilide and its Relation to Amidoazobenzene." II. By R. J. Friswell and A. G. Green.

81. "Determinations of Vapour-pressures of Alcohols and Organic Acids, and the Relations existing between the Vapour-pressures of the Alcohols and Organic Acids." By Arthur Richardson, Ph.D., University College, Bristol.

82. "The Magnetic Rotation of Mixtures of Water with some of the Acids of the Fatty Series, with Alcohol and with Sulphuric Acid; and Observations on Water of Crystallisation." By W. H. Perkin, Ph.D., F.R.S.

83. "Trimethyldiethylamidobenzene." By R. F. Ruttan, B.A., M.D., Lecturer on Chemistry in McGill University, Montreal.

84. "The Action of Bromine on Phosphorus Trichloride." By A. L. Stern, Scholar in the Chemical Laboratory of the Mason College, Birmingham.

85. "The Electrolytic Preparation of Vanadious Sulphate." By J. T. Bricrley, Dalton Chemical Scholar, Owens College.

November 4th, 1886. W. Crookes, Esq., F.R.S., Vice-President, in the Chair.

Messrs. H. Crompton, G. Dyson, T. B. Tyson and S. Williamson were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. James A. Audley, Ladderedge, Stoke-on-Trent; Chichester A. Bell, B.A., 54, Warwick Gardens, Kensington, W.; John Williams Bevan, Southview House, Shirehampton, N. Bristol; William Beecroft Bottomley, 26, Thorngate Road, Paddington; Cuthbert Robert Blackett, Fitzroy, Melbourne; Ebenezer John Cox, 23, Albany Road, Harborne, Birmingham; John Fuller, Rookwood, Chapter Road, Willesden Park; Alexander Galt, 61, Sardinia Place, Hillhead, Glasgow; Thomas Forrest Garvin, Colombo, Ceylon; Henry John Hardy, 163, Edmund Road, Sheffield; Sydney Joseph Harris, Wedgewood Institute, Burslem, Stoke-on-Trent; George Crompton Holt, Green Bank, Lawton, Kidsgrove, Stoke-on-Trent; H. E. Kirby, Kelsey Park, Beckenham, Kent; Henry A. B. Leissner, 8, Loftus Street, Sydney, N.S. Wales; Walter Leach, 27, St. Andrew's Place, Bradford; Hugh O'Donaghue Macan, B.A., Park Villa, St. Leonard's Road, Exeter; James B. L. Mackay, Trinity College, Melbourne; James B. Mackintosh, School of Mines, New York; Edward Lloyd Marks, Melbourne; Mu N. A. F. Moos, Poona, India; Herbert Pilkington, Tipton Green Furnaces, Tipton; L. S. M. Pyke, Devonshire Place House, Regent's Park, N.W.; Edwin Guayle, Glebe Point, Sydney; James Schleselman, Dundee; Harry Silvester, Roskhedyn, Broughton, Wrexham; Joseph Stapleton, 3, Lower Sackville Street, Dublin; Alfred Hughes Twining, Salcombe, Knightsbridge, Devon; Arthur Turner, The Limes, Aylesbury; William Walker, Junr., Saltburn-by-the-Sea; Reginald Williams, The Green, Norton, Stockton-on-Tees.

The following papers were read:

86.* "The Action of Chlorosulphonic Acid on Naphthalene-α- and β-Sulphonic Acids." By Henry E. Armstrong and W. P. Wynne, B.Sc.

* Communications 86 to 91 are Nos. 1 to 6 from the Chemical Department of the City and Guilds of London Institute Central Institution, South Kensington.

The investigation recorded in this paper is an extension of that of Armstrong and Graham on the action of sulphuric acid on naphthalene (Trans., 1881, 133; *Ber.*, 1882, 204). The separation of the products of the action of sulphuric acid proving a matter of great difficulty, it was judged expedient to postpone their study until further knowledge of the naphthalenedisulphonic acids had been obtained, and with this end in view such acids have been prepared by reactions in which the possibility of secondary changes taking place, such as readily occur on heating with sulphuric acid, is reduced to a minimum.

When naphthalene and SO_3HCl react in the proportion of molecule to molecule, naphthalene-α-sulphonic acid is alone produced; it is therefore only necessary to use double this proportion of chlorosulphonic acid, and the operation becomes equivalent to that of sulphonating the α-monosulphonic acid. It is desirable to add a slight excess of SO_3HCl, as some disulphochloride is formed; the naphthalene may be dissolved in CS_2, which is subsequently distilled off on the water-bath, or the chlorosulphonic acid may be added directly to the naphthalene. No higher acid is formed, even when a considerable excess of SO_3HCl is used, at temperatures not exceeding 100°. To isolate the disulphonic acid, the product is neutralised with lead carbonate, and the dried and finely divided lead salt is exhausted with hot spirit; the portion thus extracted is lead naphthalene-α-sulphonate; the residue consists of the disulphonate.

The acid thus prepared—no evidence of the presence of isomers has been obtained—differs from the two disulphonic acids of Ebert and Merz; its (sulpho)chloride melts at 184°, and on treatment with PCl_5 yields γ-dichloronaphthalene (Armstrong and Graham), so that the acid is probably the $\alpha^1\alpha^{4'}$ modification. It may be termed *γ-naphthalenedisulphonic acid.* The lead, calcium and barium salts very closely resemble the corresponding salts of Ebert and Merz's β-acid, which there is reason to believe is the symmetrical or $\beta^2\beta^{3'}$ modification, dissolving very sluggishly in water, and parting with their water of crystallisation only at a high temperature and slowly. The potassium and sodium salts (each containing 2 mols. Aq.) crystallise well, especially the latter, which forms glistening well-defined plates; although easily soluble in water, they are less soluble than the same salts of Ebert and Merz's α-acid.

Naphthalene-?-β-disulphonic Acid.—This acid appears to be the sole product of the action of SO_3HCl, on potassium naphthalene-β-monosulphonate. The chloride is added in the proportion of 3 mols. to 1 mol. of the dry salt, it being advantageous to employ a considerable excess of SO_3HCl in order to obtain a liquid product, and finally heat is applied by means of a water-bath; as a rule it is only necessary

to heat during a few minutes to ensure the whole of the salt being attacked. More or less sulphochloride is formed, the amount depending on the time during which heating takes place. Water is cautiously added to the product, and the acid potassium sulphate which separates after a time is filtered off; the remaining dissolved sulphate is separated by evaporating on the water-bath and adding spirit to the residue.

The *barium* salt, $C_{10}H_6(SO_3)_2Ba + 4OH_2$, and the potassium salt, form granular masses very similar to the corresponding β-monosulphonates in appearance and solubility; the sodium salt, $C_{10}H_6(SO_3Na)_2{\cdot}7OH_2$, forms long needles, very soluble in water. The sulphochloride is very soluble in benzene, but crystallises well from a mixture of benzene and shale spirit in aggregates of short prisms, and melts at 128—129°.

87. "The Action of Bromine on (Schaefer's) Betanaphtholsulphonic Acid." By Henry E. Armstrong and F. W. Streatfeild.

As end product of the action of bromine on $C_{10}H_6(OH){\cdot}SO_3K$, Armstrong and Graham obtained a yellow salt of the formula $C_{10}H_4BrSO_6K$, and from the manner in which it was produced they were led to regard it as a *bromoxylnaphthaquinonesulphonate*, $C_{10}H_4(O_2)(OBr){\cdot}SO_3K$, rather than as a *naphthaquinonebromohydroxysulphonate*, $C_{10}H_3Br(O_2)(OH){\cdot}SO_3K$; a small quantity of a yellow crystalline body was produced simultaneously but was not examined.

The authors have further studied these products. On adding barium chloride to a boiling solution of the potassium salt, a garnet-red salt crystallised out, which after dehydration contained 29·18 per cent. barium, corresponding with the formula $C_{10}H_3BrSO_6Ba$; on treatment with acid this is converted into a yellow monobarium salt, $(C_{10}H_4BrSO_6)_2Ba$. The production of these two salts leaves no doubt that the potassium salt is a *naphthaquinonebromohydroxysulphonate*.

The yellow bye-product is found to be *dibromohydroxynaphthaquinone*, $C_{10}H_3Br_2(O_2){\cdot}OH$.

The authors have discovered tetrabromonaphthol to be a (third) product of the action of bromine on Schaefer's salt. They find also that it is possible to prepare what appears to be a tribromonaphtholsulphonate by the action of bromine on potassium betanaphtholsulphonate dissolved in boiling muriatic acid. By oxidation of Schaefer's acid they have obtained a sulpho-acid—probably β-sulphophthalic acid: the experiments were made before the publication of those of Graebe and Rée, and it remains to identify the oxidation product with the β-sulpho-acid described by these chemists; the results, however, serve to confirm those of Claus and leave no doubt that Schaefer's acid is a *heteronucleal* di-derivative of naphthalene.

88. "The Action of Bromine on the Naphthalenesulphonic Acids." By Henry E. Armstrong and W. P. Wynne, B.Sc.

As a general result of their experiments, the authors conclude that all the *heteronucleal* naphthalenesulphonic acids, or heteronucleal naphthalenesulphonic-derivatives, yield as end product, on treatment with bromine, a bromine-derivative of either naphthaquinonesulphonic acid, or of naphthaquinone.

From the potassium salt of Ebert and Merz's β-disulphonic acid they have obtained a salt crystallising in well-defined yellow plates, of the formula $C_{10}H_3Br_2(O_2)\cdot SO_3K$ (found K = 8·69, Br = 37·05; theory K = 8·98 Br = 36·87). The α-salt of these chemists yields what appears to be an isomeric dibromonaphthaquinonesulphonate, crystallising in very soluble pale-yellow needles (found K = 8·63).

Potassium naphthalene-β-monosulphonate is first converted into the dibromosulphonate described by Jolin; on further treatment this yields what appears to be a tetrabromonaphthalenesulphonate, a brominated quinonesulphonate and tetrabromonaphthaquinone.

The authors' ?-β-disulphonate is first converted into a dibromomonosulphonate isomeric with that prepared from the β-monosulphonate; on further treatment this yields the same product apparently as Jolin's isomeric salt.

Potassium naphthalene-α-monosulphonate is known to yield dibromonaphthalene (m. p. 81°) as chief product on bromination. From their γ-disulphonate the authors have obtained a dibromomonosulphonate, two salts—each of which gives results on analysis indicating that they are dibromoquinonesulphonates, dibromonaphthaquinone, and a substance which appears to be hexabromonaphthalene; these two last are the chief products.

Hence it appears that an α-sulphonic radicle is readily displaced by bromine, but that a β-sulphonic radicle resists displacement (probably) until the nucleus in which it is contained undergoes oxidation.

89. "α-Nitro-, α-Bromo-, and α-Chloronaphthalenesulphonic Acids." By Henry E. Armstrong and S. Williamson.

As such different results are obtained on sulphonating naphthalene under various conditions, it appeared desirable to acquire further information regarding the behaviour of naphthalene-derivatives towards sulphonating agents.

α-Nitronaphthalenesulphonic acid has been prepared by Cléve from nitronaphthalene and fuming sulphuric acid; it corresponds to γ-dichloronaphthalene, and is therefore, in all probability, the $\alpha^1\alpha^4$ modification. The authors find that the same acid may readily be prepared by means of ordinary sulphuric acid, or by the action of SO_3HCl;

they have not met with an isomer. The potassium salt is remarkably stable in presence of bromine, and no well-defined product is obtained by heating an aqueous solution with bromine at 100°; but on evaporating the resulting yellow solution a deep purple-red coloured liquid is obtained. On distilling the potassium salt with $K_2Cr_2O_7$ and muriatic acid, a mixture of an almost colourless chloronitronaphthalene (m. p. 111°) with a dichloronitronaphthalene (m. p. 85°) passes over; a dibromonitronaphthalene is formed on similar treatment with $K_2Cr_2O_7$ + HBr.

When bromonaphthalene is sulphonated by means either of H_2SO_4 or SO_3HCl, it yields, together with $\alpha'\alpha^4$ $C_{10}H_6Br{\cdot}SO_3H$, which is already well known and is the chief product, an isomeric acid, the salts of which are much more soluble than those of the 1 : 4 acid; the chloride of this acid crystallises from benzene in long prisms melting at 151°.

Chloronaphthalene in like manner yields a small amount of an isomer of the 1 : 4 acid when sulphonated by SO_3HCl; the salts of the new acid are easily soluble; its chloride crystallises from a mixture of benzene and shale spirit in clusters of short thick prisms melting at 127°.

1 : 4 Chloronaphthalenesulphonic acid is readily attacked by bromine, and the 1 : 4 bromo-acid by chlorine ($K_2Cr_2O_7$ and HCl), both yielding the 1 : 4 bromochloronaphthalene (m. p. 67°) described by Guareschi.

On treatment with bromine, 1 : 4 bromonaphthalenesulphonic acid is for the most part converted into 1 : 4 dibromonaphthalene (m. p. 81°), but this is not the only bromonaphthalene produced; moreover, a portion is converted into a quinonesulphonate such as is referred to in the preceding note.

90. "The Hydrolysis of Sulphonic Acids." By A. K. Miller, Ph.D.

On page 93 of this year's *Berichte*, Kelbe states that the method of hydrolysis described by Professor Armstrong and the author (Trans., 1884, 148), yields unsatisfactory results, especially when applied to the decomposition of bromotoluenesulphonic acid and similar compounds. He introduces a modification consisting in the employment of superheated steam, which, he maintains, so far improves the method that excellent results are obtained even with the sulphonic acids of brominated hydrocarbons. The author describes experiments on the recovery of orthobromotoluene from its sulphonic acid, the results of which show that Kelbe's modification is a complication rather than an improvement, the percentage yield of bromotoluene when steam at 100° was employed being equal to the percentage yield in the experiments described by Kelbe.

91. "The Action of Bromine on Tolueneparasulphonic Acid." By the same.

The bromotoluenesulphonic acid used in the experiments mentioned in the previous notice was prepared by heating an aqueous solution of potassium tolueneparasulphonate with bromine. Potassium orthobromotolueneparasulphonate [$CH_3 : Br : SO_3K = 1 : 2 : 4$] was found to be the chief product, but besides this parabromotoluene and parabromobenzyl bromide were obtained, together with an oil which is thought to be orthoparadibromotoluene, and a solid substance melting at about 250°, the composition of which has not yet been determined.

Discussion.

Dr. Perkin remarked that a method capable of yielding a pure bromo-derivative such as orthobromotoluene would be of value; he had recently prepared bromobenzene from aniline by Sandmeyer's process, and had found that it contained a sufficient amount of impurity to affect its physical properties.

Dr. Armstrong said that the orthobromotoluene obtained by Dr. Miller had a constant boiling point. He would recommend Dr. Perkin to prepare bromobenzene in the ordinary way, to sulphonate it and purify by means of one of the salts, and then recover it by hydrolysis.

92. "Phosphorus Tetroxide." By T. E. Thorpe, F.R.S., and A. E. Tutton, Associate of the Normal School of Science, South Kensington.

The authors have examined the product formed by combustion of phosphorus in a limited supply of air, with especial reference to the statements of Reinitzer (*Ber.*, 1881, **14**, 1884) that when dissolved in water, under certain conditions, it gives a solution of a light-yellow colour, and that after dialysis this liquid is found to contain a body of perfectly neutral reaction, and coagulates on being heated to 80° after addition of a few drops of a mineral acid.

The authors, having repeated Reinitzer's experiments, are unable to confirm the existence of this so-called colloidal modification of phosphorous oxide. The yellow colour of the solution is due to the presence of the phosphorous suboxide of Le Verrier as an extremely finely divided powder, which can be removed from the liquid by repeated filtration. The colourless solution has a strong acid reaction, shows no turbidity on heating to 80°, and gives all the reactions of phosphorous acid.

When the mixed products of combustion of phosphorus are heated *in vacuo* to about 290—300°, phosphorous suboxide is formed, together with a sublimate of colourless, transparent, rhombic crystals.

These crystals sublime *in vacuo* at 180°, and are extremely deliquescent; they dissolve in water with formation of a solution of orthophosphoric and phosphorous acids, and on analysis give numbers agreeing with the formula P_2O_4. From the mode of action of water upon it, which is analogous to that of water upon N_2O_4, the authors are inclined to believe that this substance is the true tetroxide of phosphorus, and not the anhydride of the so-called phosphorosophosphoric acid, or hypophosphoric acid, discovered by Salzer.

93. "Conversion of Ditolane-azotide into Diphenanthrylene-azotide." By Francis R. Japp, F.R.S., and Cosmo Innes Burton, B.Sc.

In a previous communication on the ammonia-derivatives of benzoïn (*ante*, p. 203), Japp and Wilson showed that the so-called "benzoïnimide" of Erdmann, to which this author assigned the formula $C_{14}H_{11}N$, had in reality the formula $C_{28}H_{20}N_2$. They proposed to call it *ditolane-azotide*, and regarded it as an analogue of diphenanthrylene-azotide, $C_{28}H_{16}N_2$. A confirmation of this view would be found, if it were possible to convert the two tolane-groups in ditolane-azotide into two phenanthrylene-groups and thus obtain diphenanthrylene-azotide. Following the analogy of Graebe's synthesis of phenanthrene from stilbene, the authors therefore passed the vapour of ditolane-azotide through a red-hot tube; but only a small quantity of tarry product was obtained. However, by passing the vapour of the compound over heated soda-lime a distillate was obtained, from which diphenanthrylene-azotide, with all its characteristic properties, could be isolated. This result was confirmed by the analysis of the compound.

94. "A Chemical Study of Vegetable Albinism. Part III. Experiments with *Quercus rubra*." By A. H. Church, Professor of Chemistry in the Royal Academy of Arts.

In previous papers (Trans., 1879, 33; 1880, 1) the author has called attention to conspicuous chemical differences between the white and green foliage of seven distinct plants; in the present communication he describes the results of his study of the foliage from a large albino bough on a fine and old specimen of the scarlet oak of North America in the Royal Gardens, Kew, pointing out that they confirm and extend his previous conclusions. Leaves from the albino bough and from a contiguous green bough, collected on August 17th, 1880, gave the following results:—

	White.	Green.
Water	72·69	58·08
Organic matter	24·65	40·33
Ashes	2·66	1·59
,, from leaves dried at 100°	9·73	3·79
K_2O in ashes from dried	51·28	25·62
P_2O_5 leaves	14·64	17·05

The ashes from a larger quantity of leaves collected on July 30th, 1886, were analysed with the following results:—

	White.	Green.
Ashes from dried leaves	8·33	3·85
100 parts ashes contained:—		
K_2O	49·38	29·10
CaO	8·25	24·50
MgO	6·52	9·55
Fe_2O_3	0·82	1·24
Mn_3O_4	2·08	2·36
P_2O_5	14·25	15·80
SO_3	7·18	10·05
Cl	4·25	1·25
SiO_2	3·15	4·25
	95·88	98·10
Deduct oxygen for chlorine.	0·96	0·32
	94·92	97·78
CO_2, Na_2O, &c., by difference	5·08	2·22
Total nitrogen	3·94	2·78
Albuminoïd nitrogen	2·65	2·41
Non-albuminoïd nitrogen	1·29	0·37

The respiration and transpiration of the two kinds of leaves were also studied.

Discussion.

Mr. Warington said that the key to the difference in composition between the white and green leaves lies apparently in the fact that the former do not assimilate carbon but live practically a parasitic life. The same root-sap being primarily supplied to both kinds of leaves, the white must be richer in sap-constituents, as they contain a larger proportion of water. This fact, however, only partly explains the great preponderance of potash and other sap-constituents in the white leaves. We must further recollect that the sap of the green leaves has done far more work than the sap of the white leaves,

its active constituents have indeed been consumed for the formation of tissue. The green leaves contain far more organic matter than the white; but this corresponds to only a small part of the work done. The green leaves have, in fact, furnished organic matter for the nourishment of the whole tree, and the organic substances transferred from the leaves to form woody tissue have doubtless been accompanied by the necessary sap-constituents. The sap of the green leaves is thus to a great extent exhausted sap. One constituent, however, preponderates in the green leaves, viz., lime. Salts of calcium occur largely as encrusting matter in old leaves; these salts have accumulated more in the green leaves, as a result of greater evaporation from the surface, and probably, from the removal of the carbon dioxide which held them in solution. In the white leaves there has been less evaporation, and a production instead of removal of carbon dioxide.

95. "The Synthetical Formation of Closed Carbon-chains. Part II. Some Derivatives of Tetramethylene." By W. H. Perkin, Jun., Ph.D.

In a previous paper (Trans., 1885, 801) the author has shown that if the sodium compound of ethylic malonate be treated with ethylene-bromide, ethylic trimethylenedicarboxylate (1, 1), $\left.\begin{matrix}CH_2\\CH_2\end{matrix}\right\}C(CO_2Et)_2$, is formed. The action of trimethylene bromide on ethylic sodiomalonate has now been studied, and the derivatives of tetramethylene thus obtained are described in the paper.

The first product of the reaction is ethylic tetramethylenedicarboxylate, $\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot C(COOEt)_2\end{matrix}$, which is a colourless oil, boiling at 223°. On hydrolysis this salt is converted into tetramethylenedicarboxylic acid (1, 1) (m. p. 154—156°), which in its turn is easily converted on heating into tetramethylenecarboxylic acid, $C_4H_7\cdot COOH$ (b. p. 191°), and carbonic anhydride.

A second method of synthesising tetramethylene-derivatives is the following:—

The product of the action of one molecular proportion of ethylene-bromide and two molecular proportions of ethylic malonate is ethylic butane - $\omega_2\omega_2$ - tetracarboxylate, $(CO_2Et)_2CH\cdot CH_2\cdot CH_2\cdot CH(CO_2Et)_2$. When this salt is treated with sodium it forms a disodium-derivative, which by the action of bromine is easily converted into ethylic tetramethylenetetracarboxylate (1, 1, 2, 2), $\begin{matrix}CH_2\cdot C(COOEt)_2\\CH_2\cdot C(COOEt)_2\end{matrix}$.

Tetramethylenetetracarboxylic acid is a colourless crystalline mass, melting at 145—150°. On heating it is easily converted into tetra-

methylenedicarboxylic acid (1, 2) (m. p. 130°) and carbonic anhydride. The anhydride of this latter acid (m. p. 76—78°) is obtained by heating the acid to 300°.

Diacetyltetramethylenedicarboxylic acid, $\begin{matrix}CH_2\cdot CAc\cdot COOH\\CH_2\cdot CAc\cdot COOH\end{matrix}$, is obtained in a similar way from the product of the action of one molecular proportion of ethylene bromide and two molecular proportions of ethylic acetoacetate. It is a colourless crystalline mass melting at 210°.

96. "The Action of the Halogens on the Salts of Organic Bases. Part II. Tetramethylammonium Salts." By Leonard Dobbin, Ph.D., and Orme Masson, M.A., D.Sc., Chemical Laboratory of the University of Edinburgh.

The actions of the halogens on the tetramethylammonium salts pretty closely resemble those on the trimethylsulphine salts described in a previous paper.

Of the addition products obtained from haloid tetramethylammonium salts, those which contain one atom of iodine are brightly coloured crystalline compounds of considerable stability. The crystals of the dibromiodide, Me_4NIBr_2, are orange, and those of the dichloriodide, Me_4NICl_2, are yellow. Both of these substances, like the corresponding trimethylsulphine-derivatives, take up ammonia gas, the dichloriodide doing so more readily than the dibromiodide.

A chlorobromiodide was not obtained by acting on tetramethylammonium bromide with iodine monochloride, but a dichloriodide was formed, the bromine being displaced by chlorine. In this respect the tetramethylammonium series differs from the trimethylsulphine series.

Those addition products which contain only bromine or chlorine, or both, are very unstable substances, and rapidly lose halogen in air, leaving haloid salts. Some of these were obtained in crystals but not in a pure state, being always mixed with some haloid salt.

An experiment in which tetrethylphosphonium iodide was acted on by bromine proved that the reaction took place in the case of the phosphorus bases also, a crystalline product being obtained.

97. "Glycyphyllin, the Sweet Principle of *Smilax glycyphylla*." By Edward H. Rennie, M.A. (Sydney), D.Sc. (London), Professor of Chemistry in the University of Adelaide, South Australia.

Smilax glycyphylla is a plant which grows in abundance on the shores of Port Jackson, and is common on the coasts of the northern

parts of New South Wales and the southern parts of Queensland; the sweet principle extracted from its leaves has already been partially examined by Dr. Wright and the author (Trans., 1881, 237). The author now corrects the formula previously given to $C_{21}H_{24}O_9$: glycyphyllin separates from aqueous ether with three, and from water with four and a half molecules of water of crystallisation. On hydrolysis, it yields *phloretin* and *isodulcite*: $C_{21}H_{24}O_9 + 2H_2O = C_{15}H_{14}O_5 + C_6H_{14}O_6$, and is therefore closely allied to phlorizin, with which it is proposed to carefully compare it.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Canadian Economics, being Papers prepared for reading before the Economical Section of the British Association for the Advancement of Science at the Montreal Meeting, 1884: Montreal, 1885: from the Montreal Committee.

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Verhandlüngen der Kaiserlich Leopoldinisch Carolinischen Deütschen Akademie der Naturforscher: Bände 47 and 48: Halle, 1885–6: from the Academy.

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Versuche über die Platina, 1782.

A century of the names and scantlings of Inventions: by the Marquis of Worcester; reprint: London, 1786.

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Miscellaneous Papers, collected by Dr. Flight, bound in 7 vols.

At the next meeting, on November 18th, there will be a ballot for the election of Fellows, and the following Papers will be read:—

"On the Preparation and Hydrolysis of Hydrocyanides of the Diketones." By Francis R. Japp, F.R.S., and N. H. J. Miller, Ph.D.

"A Spectroscopic Study of Dyes and Colours. Note on Naegeli's Theory of Fermentation." By W. N. Hartley, F.R.S.

"The Reduction of Nitrites to Hydroxylamine by Hydrogen Sulphide." By E. Divers, F.R.S., and Tamemasa Haga.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 28. Session 1885–86.

November 18th, 1886. W. Crookes, Esq., F.R.S., Vice-President, in the Chair.

Mr. A. Wentworth Jones was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Horace Edward Brothers, Zaffre Cottage, Solden Hill, Stoke-on-Trent; Francis James Henderson Coutts, 61, East View, Turton Road, near Bolton; Tamemasa Haga, 1, Sadowara-machi, Itchomé, Tokyo, Japan; Michitada Kawakita, Engineering College, Tokyo, Japan; Stephen James Pentecost, Nottingham Road, New Basford, Nottingham; Henry Joshua Phillips, G.W.R. Laboratory, Swindon; P. Yeshwant Sheshadri, Jalua, Bombay, India; Tetsukichi Shimidzu, Noshomusho, Tokyo, Japan; William Phillips Thompson, 95, Shrewsbury Road, Birkenhead; Hikorokurō Yoshida, Science College, Imperial University, Tokyo, Japan.

The following were elected Fellows of the Society:—

Messrs. B. F. Davenport, M.A., M.D.; W. Ralph Dodd; Laurence Hislop; A. B. Lyons, A.M., M.D.; James B. Readman; Alfred Rée; V. Phelps Richard; F. T. Shutt, B.A.; Edgar F. Smith, Ph.D.

The following papers were read:—

98. "Researches on the Relation between the Molecular Structure of Carbon Compounds and their Absorption Spectra. Part VIII. A Study of Coloured Substances and Dyes." By W. N. Hartley, F.R.S., Royal College of Science, Dublin.

The author refers to a paper by Dr. Otto N. Witt, published in 1876, in which it is stated that the tinctorial characters of benzenoid

compounds is conditional upon the simultaneous presence in the molecule of a colour-producing group and a salt-forming group of atoms: a group of atoms of the former kind being designated a *chromogen*, and of the latter a *chromophor*. He has studied the relation of the hydrocarbons to the more complex compounds which are colouring matters derived therefrom. It is shown that benzene and the derived hydrocarbons have the property of selecting and absorbing certain rays of the spectrum, and may thus be regarded as coloured bodies, the colours of which are too subtle for the eye to perceive them. By certain reactions, two or more benzenes may be linked in such a way that the rate of vibration of the new molecule is reduced so that it absorbs rays within the region of visibility. That which has been called a chromogen is an invisibly coloured substance, and that which is termed a chromophor is an atom or group of atoms capable of so reacting as to reduce the rate of vibration of the molecule, with the result that it absorbs rays of no higher refrangibility than the violet. Under certain conditions oxygen and nitrogen are chromophors, hence also hydroxyl and nitroxyl.

The spectrum measurements of a number of nearly related dyes and colouring matters are given, together with diagrams indicating their molecular vibrations.

The modification seen in the curve of benzene when an alkyl radicle displaces hydrogen consists in three out of the four absorption-bands being merged in one, and the rate of vibration of the absorbed rays is less.

When a body like triphenylmethane is examined, the absorption curve has much of the general character of that of benzene, but the modifications which it has undergone are much like what one might expect from its constitution. First, there is one broad band of absorption with just an indication of a second being merged in this. Secondly, a great increase in the amplitude of the vibrations. Thirdly, the rate of vibration of the absorbed rays is greatly reduced.

When magenta, Hofmann's violet, and iodine-green are examined it is seen that the curves are modifications of that of triphenylmethane; they follow each other closely, but the molecule of greatest mass transmits least light, and the light is composed of rays vibrating with least rapidity, thus indicating a greater amplitude and less rapidity of vibration of the molecule.

Azobenzene and a number of its derivatives of very varied constitution exhibit curves remarkably similar.

It is remarked that when absorption takes place in the visible region the ultra-violet rays are generally completely absorbed.

99. "Spectroscopic Notes on the Carbohydrates and Albumenoids from Grain." By W. N. Hartley, F.R.S., Royal College of Science, Dublin.

According to C. v. Naegeli ("Theorie der Gährung") fermentation is a process which may be described as the transference to fermentable matter of the molecular or rather intra-molecular vibrations of the different constituent substances entering into the composition of living protoplasm (which remains itself unchanged in composition), and hence the equilibrium of the molecules of the fermentable matter becomes so disturbed as to cause their resolution into simpler molecules. The author has had recourse to spectrum observations, in order to obtain, if possible, some information as to the mode and rate of vibration of the molecules of the bodies which initiate and participate in fermentative changes.

It is pointed out that animal albumens of various kinds examined by M. L. Soret are distinguished by absorption-bands produced by small thicknesses of dilute solutions, while the albumenoids invertase and diastase, and the water in which yeast has been washed, afford solutions which are very diactinic, and as far as could be ascertained do not exhibit absorption-bands. Moreover, gelatine is very diactinic when quite pure, and so also are the carbohydrates starch, cane-sugar, and glucose. It does not therefore appear that there is anything in the mode and rate of vibrations of invertase which is incompatible with a transference of its vibrations to glucose, nor of the vibrations of diastase to starch; hence it is possible that some material within the yeast cell may communicate its motion to the sugar outside of it and so resolve the complex molecule into simpler molecules. Putting the theory of fermentation on one side, it is of interest to know that the facility with which the ultra-violet rays traverse solutions of the carbohydrates is quite in accord with what we know of their constitution, notwithstanding the complexity of their molecules. It is further no less interesting to know that the albumenoids associated with the carbohydrates are evidently of very different constitution from those found in the animal organism. It is pointed out that gelatine dry plates very rarely receive impressions of rays of higher refrangibility than 2146, and this is due to some slight impurity in the gelatine, since some specimens of gelatine transmit the line of zinc 2024.

Discussion.

Mr. Spiller, referring to the differences in sensibility of gelatine plates to the most refrangible rays commented on by Professor Hartley, said that owing to the difficulty experienced in getting silver bromide emulsion to set and dry sufficiently rapidly in summer time, it

had sometimes been the practice of makers to add a minute proportion of chrome-alum: this might account for some of the differences observed.

Professor Hartley said that he had long thought that the soluble bromides had not been completely washed out, but as plates prepared with special care for him by Messrs. Mawson and Swan had also manifested the differences described, he now thought that they were probably due to actual differences—some minute impurity—in the gelatine used at different times in preparing the plates.

100. "Preliminary Note on the Electrolysis of Ammonic Sulphate." By Herbert McLeod, F.R.S.

When a neutral solution of ammonic sulphate is electrolysed in a U-tube provided with platinum plates as electrodes, nearly pure oxygen is evolved at the positive pole and hydrogen at the negative. For one volume of gas from the positive pole, a quantity varying between 4·7 and 5·4 volumes is evolved from the negative pole. A small amount of ozone is produced. On mixing together the electrolysed liquid at the poles a strongly alkaline liquid is obtained, containing a considerable quantity of "active" oxygen. When the liquid is first neutralised with sulphuric acid, then treated with excess of baric chloride, and the baric sulphate filtered off, the liquid deposits baric sulphate on boiling, an indication of the presence of persulphuric acid in the solution.

When sulphuric acid that has been electrolysed is exactly neutralised with baric hydrate, the precipitate filtered off and the liquid boiled, baric sulphate is precipitated; at the same time the liquid becomes acid and a further quantity of baric sulphate is thrown down on the addition of baric chloride.

Discussion.

In reply to a question by the President, Professor McLeod said that Faraday in the experiments which gave results differing from those now described, had used an alkaline solution of ammonium sulphate in ammonia.

Dr. Messel asked if the deficiency in oxygen might not be due to the formation of hydrogen peroxide. In experiments on the electrolysis of sulphuric acid solution (with a current of 60 amperès), he had at all events observed the characteristic colour on application of the chromic acid and ether test.

Professor McLeod said that he had always failed to detect hydrogen peroxide.

101. "The Preparation and Hydrolysis of Hydrocyanides of the Diketones." By Francis R. Japp, F.R.S., and N. H. J. Miller, Ph.D.

The authors have attempted to hydrolyse Zinin's benzil-dihydrocyanide, $C_{14}H_{10}(OH)_2(CN)_2$, by means of concentrated chlorhydric acid, but without success. However, by dissolving benzil in alcohol, adding an excess of hydrogen cyanide, saturating the liquid with hydrogen chloride, and allowing the whole to stand for some weeks, a compound of the formula $C_{16}H_{12}N_2O$ was obtained, a reducing action having taken place. The compound crystallises from benzene in lustrous yellow flat needles or laminæ, melting at 196—197°. It is feebly basic, yielding a colourless hydrochloride which is decomposed by water. At the same time an acid of the formula $C_{16}H_{13}NO_4$ was obtained.

By the action of a strong aqueous solution of hydrogen cyanide upon phenanthraquinone, a dihydrocyanide, $C_{14}H_8(OH)_2(CN)_2$, corresponding with the benzil-derivative prepared by Zinin, was obtained. It crystallised in tufts of very slender needles, which when heated decomposed with evolution of hydrogen cyanide. Treated with fuming chlorhydric acid in the cold, this compound slowly evolves carbonic anhydride, and yields a mixture of two compounds, $C_{15}H_9NO$ (needles melting at 241°) and $C_{15}H_{11}NO_2$ (needles melting at 183°).

The compound $C_{15}H_9NO$ appears to be a lactam or lactim. It unites directly with metallic hydroxides to form salts, without elimination of water, and from the solutions of these salts mineral acids precipitate the original substance. It decomposes carbonates. The compound $C_{15}H_{11}NO_2$ is an acid; its salts appear to be isomeric with those of the compound $C_{15}H_9NO$, but are so unstable that satisfactory analytical figures could not be obtained.

In a preliminary note on the above subject (*Ber.*, **16**, 2418) the authors erroneously ascribed the formulæ $C_{16}H_{11}NO$ and $C_{16}H_{13}NO_2$ to those two compounds. The difference in percentage composition between the C_{15} and C_{16} formulæ is very slight, affecting chiefly the hydrogen, which was found too high in the earlier analyses.

102. "The Action of Salicylic Aldehyde on Sodium Succinate in presence of Acetic Anhydride." By Gibson Dyson, Demonstrator of Chemistry, Normal School of Science, South Kensington.

By heating a mixture of 10 grams sodium succinate, 15 grams salicylic aldehyde, and 13 grams acetic anhydride, in a sealed tube for 40 hours, at a temperature of 140° C., the author obtained a substance having the composition $C_{18}H_{10}O_4$, to which he has given the name "*Dicoumarine*." It is an extremely stable body, insoluble in water, ether, alcohol, benzene, and chloroform, but soluble to a slight extent

in hot glacial acetic acid, from which it separates on cooling in acicular crystals. It dissolves in a hot solution of sodium hydrate, but is reprecipitated unchanged on addition of an acid.

By acting on its alkaline solution with sodium amalgam, hydrodicoumaric acid, $C_{18}H_{14}O_5$, is formed. This acid, when heated at 130° C., gives off a molecule of water, yielding an anhydride (hydrodicoumarine) $C_{18}H_{14}O_4$ (m. p. 256° C.); hydrodicoumaric acid also combines with bromine to form addition products. By further reduction of hydrodicoumaric acid, an acid having the composition $C_{18}H_{18}O_6$ is obtained. This *dihydrocoumaric acid* yields an anhydride, $C_{18}H_{14}O_4$, melting at 222—224° C.

Zwenger (*Annalen*, Sup. 8, 32), by reducing a saturated alcoholic solution of coumarine with sodium amalgam, obtained hydrocoumaric acid, $C_{18}H_{18}O_6$, which yields an anhydride, $C_{18}H_{14}O_4$, melting at 222° C. The constitution assigned by Zwenger to his acid is the same as that given by the author to dihydrocoumaric acid; the two acids are, however, not identical. Both acids yield an anhydride $C_{18}H_{14}O_4$, melting at 222° C. It is probable that we have here another case of isomerism similar to that observed by Perkin to exist betwen α- and β-coumaric acid.

103. "The Reduction of Nitrites to Hydroxylamine by Hydrogen Sulphide." By E. Divers, F.R.S., and T. Haga.

On decomposing silver nitrite with hydrogen sulphide, hydroxylamine is formed as chief product. Mercurous nitrite, supposed hitherto not to exist, has been prepared by the authors, and will be described in a future communication; it also yields hydroxylamine on treatment with hydrogen sulphide. In a preliminary note (*ante*, p. 95) reference was made to the production of yellow crystals of unknown nature, together with metallic mercury and hydroxylamine, on treating mercurous nitrate with nitric oxide: having since prepared mercurous nitrite, the authors have now learned that these yellow crystals were this salt; and having ascertained that hydrogen sulphide converts it partly into hydroxylamine, they further recognised that the apparent formation of this base from mercurous *nitrate* and *nitric oxide* had really been its formation from mercurous *nitrite* and the *hydrogen sulphide* used to remove the mercury from the solution, as mercurous nitrite is soluble in nitric acid with but partial decomposition. The green solution prepared by mixing alkali nitrite with copper sulphate also yields hydroxylamine when treated with hydrogen sulphide. Alkali nitrites alone treated with hydrogen sulphide and then acidified, yield no hydroxylamine. The formation, here described, of hydroxylamine from the nitrites of

the silver-mercury group of metals, is the only indisputable evidence there yet is of the conversion of an inorganic nitrite into hydroxylamine.

104. "Note on Some Double Thiosulphates." By J. B. Cohen, Ph.D., Assistant Lecturer on Chemistry, Owens College.

Rammelsberg found that by the action of copper sulphate upon a solution of potassium thiosulphate a cuprous potassium thiosulphate was formed of the composition $K_2S_2O_3{\cdot}Cu_2S_2O_3{\cdot}2H_2O$. By increasing the proportions of potassium thiosulphate, a hydrated and anhydrous salt of the composition $Cu_2S_2O_3{\cdot}2K_2S_2O_3{\cdot}3H_2O$ and $Cu_2S_2O_3{\cdot}2{\cdot}K_2S_2O_3$, may be obtained, both of which give the same cuprous barium thiosulphate on addition of $BaCl_2$. An anhydrous silver potassium thiosulphate of the composition $K_2S_2O_3{\cdot}2Ag_2S_2O_3$ has also been prepared.

105. "Preliminary Note on the Action of Triphenylmethyl Bromide on Ethyl Sodio-malonate." By George G. Henderson, M.A., B.Sc., Assistant to the Professor of Chemistry, University of Glasgow.

When triphenylmethyl bromide, dissolved in absolute ether, is treated for some time with an equivalent quantity of ethylic sodiomalonate, a reaction gradually takes place; *ethylic triphenylmethylmalonate* $[CH{\cdot}C(C_6H_5)_3{\cdot}(COOC_2H_5)_2]$ being formed. This substance crystallises from alcohol in colourless shining prismatic crystals which melt at 133·5°.

When hydrolysed with alcoholic potash, it is partially decomposed, arbon dioxide being split off, and the sodium salt of *β-triphenylpropionic acid* is formed. The acid itself $[C(C_6H_5)_3{\cdot}CH_2{\cdot}COOH]$ crystallises from alcohol in small colourless prisms which melt at 177°.

The sodium salt $(C_{21}H_{17}O_2Na{\cdot}H_2O)$ crystallises from water, in which it is very soluble, in long silky needles. The barium salt $[(C_{21}H_{17}O_2)_2Ba{\cdot}H_2O]$, is difficultly soluble in water, but readily soluble in alcohol, from which it separates in white crystals. The silver salt $[C_{21}H_{17}O_2Ag]$ is obtained as a white micro-crystalline precipitate, almost insoluble in water and alcohol.

106. "Action of Silicon Tetrachloride on Aromatic Amido-compounds." By Arthur Harden, B.Sc., Dalton Scholar in the Owens College.

The author finds that primary amines react with silicon tetrachloride, forming diamines of the formula $SiCl_2(NHR')_2$. He has

prepared such compounds from aniline, orthotoluidine, isoxylidine, and betanaphthylamine.

Pyridine and quinoline form the additive compounds, $2C_5H_5N{\cdot}SiCl_4$, $2C_9H_7N{\cdot}SiCl_4$.

RESEARCH FUND.

A meeting of the Research Fund Committee will be held in December. Fellows desiring grants are requested to make application before December 11th.

Titles of Papers of interest to Chemists recently read before Societies in the United Kingdom :—

"On the Action of Hydrochloric Acid Gas upon certain Metals;" and "On the Capillary Constants of Benzene and its Homologues occurring in Coal Tar." By T. B. Cohen.

Manchester Literary and Philosophical Society, Nov. 2nd.

"On the Specific Heats of Minerals." By J. Joly.

"On the Method of Condensation in Calorimetry." By J. Joly.

"A Theory of Voltaic Action." By J. Brown.

Royal Society of London, November 18th.

At the next meeting, on December 2nd, there will be a ballot for the election of Fellows, and the following Papers will be read :—

"Bismuthates." By M. M. P. Muir.

"The Action of Inorganic Compounds on Living Matter." By James Blake, M.D.

"Morindin and Morindon." By T. E. Thorpe, F.R.S., and A. T. Greenall.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 29. Session 1885–86.

December 2nd, 1886. W. Perkin, Esq., Ph.D., F.R.S., Vice-President, in the Chair.

Mr. Forbes Rickard was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Arthur Henry Downes, M.D., Chelmsford, Essex; George Arthur Goyder, Hawkers Road, Adelaide, Australia; E. Hori, 88, King Henry's Road, Chalk Farm, N.W.; Thomas Burdon Keay, 85, Herrington Street, Sunderland; Charles E. Sohn, jun., 25, Beverley Road, Anerley; James Pim Strangman, Sarno, Province of Salerno, Italy; Jokichi Takamine, Department of Agriculture and Commerce, Tokio.

The following were elected Fellows of the Society:—

Messrs. James A. Audley, Chichester A. Bell, B.A., M.B., John Williams Bevan, Cuthbert Robert Blackett, William B. Bottomley, Ebenezer John Cox, John Fuller, Alexander Galt, Thomas Forest Garwin, Sydney Joseph Harris, George Crompton Holt, H. E. Kirby, Henry A. B. Leissner, James B. L. Mackay, Hugh O'Donoghue Macan, B.A., James B. Mackintosh, Edward Lloyd Marks, N. A. F. Moos, Herbert Pickington, L. S. M. Pyke, Edwin Quayle, James Schleselman, Harry Silvester, Arthur Turner, Alfred Hughes Twining, William Walker, jun., Reginald Williams.

The following papers were read:—

107. "Bismuthates." By M. M. Pattison Muir and Douglas J. Carnegie.

The authors have attempted to isolate definite compounds of Bi_2O_5, or Bi_2O_4, with K_2O, but without success. They find that very long

continued washing with hot water is required to remove all the potash from the solid products of the reaction between BiO_3H_3 or BiOCl, very concentrated potash solution and chlorine. They show that $Bi_2O_5{\cdot}xH_2O$ dissolves in about 100 times its weight of a boiling solution of KOH in a little water, and that yellowish-white solids are obtained by nearly neutralising this solution; that these solids may be washed free from potash by boiling water, and that the residual bodies then contain more oxygen than Bi_2O_3, and nearly approach the composition Bi_2O_4. They conclude that $Bi_2O_5{\cdot}xH_2O$ exhibits feebly acidic functions in its reaction with a large mass of very concentrated potash solution; that under these conditions compounds of the form $xBi_2O_5{\cdot}yK_2O$ (or perhaps $xBi_2O_4{\cdot}yK_2O$) are probably formed, but that such compounds can only exist, if at all, in presence of large quantities of potash. The authors give reasons for regarding the formulæ given by C. Hoffmann (*Annalen*, 223, 110) to so-called potassium bismuthates as of little if any value.

108. "The Action of Inorganic Compounds on Living Matter." By James Blake, M.D.

The reactions taking place between living matter and inorganic compounds have been investigated by introducing solutions of the substances directly into the veins and arteries of living animals. The action of compounds of more than forty of the elements have been investigated, and the following conclusions have been arrived at:—1st. That the action of these substances on living matter is determined by the electropositive element. 2nd. That their general biological action is connected with their isomorphous relations, substances in the same isomorphous group causing the same biological reactions. 3rd. That in the same isomorphous group the intensity of biological action is determined by the atomic weight, the greater the atomic weight the smaller the quantity required to cause the same amount of biological action. The nature of these reactions is at present undetermined. They most probably are due to contact reactions.

Discussion.

Mr. Lloyd asked whether Dr. Blake had experimented on vegetable matter, and if so, had he obtained similar results? Potash salts appeared to have an action altogether different from that of other members of the group; and it was known also that they affected plants in a special manner.

Dr. Stevenson said that the subject of the communication was one of great interest, but beset with difficulties. Isomorphous substances often acted very differently upon the animal body, as for instance in

the cases of sodium chloride and potassium iodide. Nor would the differences in the atomic weights of potassium and sodium account for the numerous differences in the toxic properties of their salts. Zinc sulphate and ferrous sulphate are isomorphous, but their physiological actions differ greatly. The magnesium group of metals were asserted by the author to act upon the vomiting nervous centre, but whilst this might be conceded as true of zinc and cadmium salts, magnesium salts were not usually regarded as emetics. We know so little of the molecular constitution of bodies in solution, that it was hazardous to reason from the isomorphism of solids to their analogies when in solution.

Dr. Lauder Brunton regarded Dr. Blake as a pioneer in the field of pharmacology, and thought his paper interesting and instructive. The conclusions were, however, rather too general, and the exceptions deserving of more attention than Dr. Blake had given them. Thus the action of the chloride, bromide and iodide of sodium is determined rather by the electronegative than by the electropositive element, and this is still more the case with the nitrites, all of which, both organic and inorganic, cause dilatation of the blood-vessels. The first-named salts also differ in action, although isomorphous. Again the toxic power of elements does not rise regularly with their atomic weight, for sodium is less toxic than lithium; but potassium, though more toxic than sodium, is less so than rubidium. The body as a whole is a too complicated reagent, and instead of trying to arrange substances according to their lethal action on the body, a better result would be obtained, he thought, by investigating the effect of different substances on the constituent parts of the body, such as muscle, nerve, and nerve-centre.

Dr. Blake, in reply to a question by Mr. Newlands, stated that he had not experimented on the therapeutic action of boracic acid. He had never before heard of the fact mentioned by Mr. Lloyd, that potash salts exercised an abnormal action on living vegetable matter. The observation was interesting, as of all the substances experimented with the potash salts were the only ones whose biological action was not in agreement with their isomorphous relations. This fact, however, cannot be regarded as an argument against his deduction that analogous actions were produced by isomorphous compounds, which was based upon the results of the examination of the biological action of forty-two other elements, potash salts forming in fact the only exception. The statement made by Dr. Stevenson, that the bromides, iodides and chlorides of the same base differed in their physiological action, was a mistake, founded on imperfect methods of experimenting.

His own experiments, as well as those of other observers, had shown that such was not the case. The remark by Dr. Brunton as to nitrous

acid modifying the biological action of the base was undoubtedly true ; pyrophosphoric and pyrovanadic acids also exerted a modifying influence, but he had shown that the sulphates, nitrates, phosphates, arseniates, carbonates, acetates, chlorides, iodides and bromides of the same base caused the same biological reactions when introduced directly into the blood. To the remark of Dr. Stevenson that it was extremely improbable that compounds of such different elements as are contained in the same isomorphous group should cause the same reactions on the various organs, the speaker would only say that, however improbable such a fact might appear, yet experiment had clearly proved that such was the case. As an example that such was the case the action of the salts on the magnesium group was referred to, all of which act on the heart, on the vomiting centre, on the spinal cord and on the blood, in exactly the same manner.

109. "Morindin and Morindon." By T. E. Thorpe, F.R.S., and T. H. Greenall.

Morindin was discovered by Anderson in the *Surangi*, the roots of *Morinda citrifolia*, which are extensively used in India as a dye-stuff, more especially for dyeing reds, purples and chocolates. The substance occurs mainly in the root bark, and can be extracted by treatment with dilute alcohol, from which it crystallises in lustrous sulphur-yellow prisms. According to Anderson it has the formula $C_{28}H_{30}O_{15}$.

On heating in closed tubes it is decomposed, and yields a sublimate of *Morindon*, crystallising in long red needle-shaped crystals, to which Anderson assigned the formula $C_{28}H_{20}O_{10}$.

According to Rochleder and Stenhouse morindin is identical with ruberythric acid, $C_{26}H_{28}O_{14}$, and hence morindon is alizarin. Stein (*J. pr. Chem.*, **97**, 234) has, however, pointed out several facts which are inconsistent with this supposition. Morindin, like ruberythric acid, is a glucoside, but the product which it yields on hydrolysis, in addition to glucose, is not alizarin.

The authors have examined this question, and in the main their results agree with those of Stein. They extracted morindin from the roots of *Morinda citrifolia*, for a sample of which they are indebted to the Director of the Royal Gardens, Kew, and have compared its properties with those of ruberythric acid, obtained through the kindness of Dr. Schunk. The two substances are not identical, and they behave very differently on hydrolysis. Morindin gives with sulphuric acid, ferric chloride, and on treatment with nitric acid perfectly different reactions from those afforded by alizarin. The analytical numbers obtained for morindin agree closely with those of Anderson;

those obtained for morindon indicate that it is probably trihydroxymethylanthraquinone. The quantity of the two products at the disposal of the authors was insufficient to definitely settle the constitution of the substances. Through the kindness of Mr. Wardle, of Leek, they have obtained a large supply of *M. citrifolia*, and also of *M. tinctoria*, and a further communication on the subject is promised.

Discussion.

Mr. Groves said that he had assisted Dr. Stenhouse in the investigation referred to; it was not certain whether the species of *Morinda* examined was *citrifolia* or *tinctoria*. Also it was important to remember that a particular constituent might occur in a plant on one occasion and be absent in another sample, grown perhaps under somewhat different conditions. Thus Dr. Stenhouse had discovered *Munjistin* in the sample of munjeet he originally examined, but had altogether failed to find it subsequently in another sample, which, instead, contained another substance.

110. "The Hydration of Salts: Cadmium Chloride." By S. U. Pickering.

Dr. Nicol has laid considerable weight (*Chem. News*, **54**, 191) upon the fact that Thomsen (*Thermochem.*, **3**, 201) has found the heat of hydration of cadmium chloride to be a negative quantity. This being the only inorganic salt which has a negative heat of hydration, the author has repeated Thomsen's work. Two samples were prepared of anhydrous salt, one at 200° C., and the other fused; they both gave numbers practically identical with that obtained by Thomsen, at 18°, −3011 cal. The hydrated salt also gave a number very nearly the same as Thomsen's, −760 cal., but was found to be a monohydrate instead of a dihydrate. Thomsen, therefore, in describing the salt used by him as containing $2H_2O$, has evidently made some error. The monohydrate is obtained upon evaporating a hot solution, and the dihydrate from a cold solution only. The dihydrate gives −2284 cal. on dissolution, and hence the heat of hydration of the salt is $CdCl_2{\cdot}H_2O$ (solid) = 1092 cal., and $CdCl_2{\cdot}2H_2O$ (solid) = 2421 cal.

111. "The Decomposition of Sodium Carbonate on Fusion." By S. U. Pickering.

The author has investigated sodium carbonate in the manner in which he investigated sodium sulphate (*Chem. Soc. Trans.*, 1884, 686), with a view to asertain whether the discrepancies in the numbers given for its heat of dissolution could be accounted for by its

existence in two modifications, as in the case of the sulphate. All specimens dehydrated at temperatures below the fusing point of the salt gave identical numbers, but the fused salt gave a result 200 cal. higher; this was traced to the decomposition of the carbonate: for on exposure to carbon dioxide that gas was absorbed, and the salt then gave a heat of dissolution 600 cal. less than the normal, owing to the formation of some of the acid carbonate, the necessary hydrogen having been derived from atmospheric moisture absorbed by the decomposed carbonate during its preparation. The amount of carbonate decomposed on simple fusion was about 3 *per cent.*

112. "Derivatives of Tolylbenzene." By Thomas Carnelley, D.Sc. (Lond.) and Andrew Thomson, D.Sc. (Edin.).

The preparation and properties of the following compounds are described:—

1. α-Monobromotolylbenzene, $C_6H_5{\cdot}C_6H_3Br{\cdot}CH_3 = 1:(2 \text{ or } 3):4$, m. p. 127—129°.

2. β-Monobromotolylbenzene, $C_6H_4Br{\cdot}C_6H_4{\cdot}CH_3 = 1:4—1:4$, m. p. 27—30°.

3. β-Monobromophenylbenzoic acid, $C_6H_4Br{\cdot}C_6H_4{\cdot}COOH = 1:4—1:4$, m. p. 193—194°.

4. α-Dibromotolylbenzene, $C_6H_4Br{\cdot}C_6H_3Br{\cdot}CH_3 = 1:4—1:(2 \text{ or } 3):4$, m. p. 113—115°.

5. α-Bromophenylbromobenzoic acid, $C_6H_4Br{\cdot}C_6H_3Br{\cdot}COOH = 1:4—1:(2 \text{ or } 3):4$, m. p. 202—204°.

6. β-Dibromotolylbenzene, $C_6H_4Br{\cdot}C_6H_3Br{\cdot}CH_3 = 1:4—1:(3 \text{ or } 2):4$, m. p. 148—150°.

7. β-Bromophenylbromobenzoic acid, $C_6H_4Br{\cdot}C_6H_3Br{\cdot}COOH = 1:4—1:(3 \text{ or } 2):4$, m.p. 231—232°.

Terephthalic acid was obtained as the final oxidation product of α-monobromoditolylbenzene, and parabromobenzoic acid as the final oxidation product of β-monobromotolylbenzene and of α- and β-dibromotolylbenzene.

The two bromophenylbromobenzoic acids, melting respectively at 202—204° and 231—232°, are isomeric and not identical with the dibromophenylbenzoic acid described by Hohn (*Ber.*, **16**, 1082) since his acid was obtained from β-dibromofluorene ketone, and is therefore a derivative of 1:2 phenylbenzoic acid, whereas both our acids are derived from 1:4 phenylbenzoic acid.

113. "The Amount of Chlorine in Rain-water collected at Cirencester." By Edward Kinch, Royal Agricultural College, Cirencester.

Determinations of chlorine in the rain-water collected in a small 5-inch rain gauge, at the Royal Agricultural College, 443 feet above

the mean sea-level, have been made continuously since 1870. The rain collected during the six months April to September is kept apart from that of the six winter months October to March; the chlorine is determined in the mixed waters of each six months.

The amount of chlorides in the rain is nearly always greater in the winter months than in the summer months. An abnormal amount of chlorides can generally be traced to storms from the south-west bringing salt spray from the Bristol Channel, about 35 miles distant. Crystals of common salt have been found after such storms on the windows of the College facing west. On one occasion, in September, 1869, Professor Church found chlorine equivalent to 6·71 grains of common salt per gallon in storm-water.

The rain collected during the winter six months, 1872–3, contained an abnormally large amount of chlorine; excluding this period the yearly averages for 16 years, 1870–1885, for the 12 years 1874–1885–86, also the means of the last 12 summer periods and 12 winter periods are—

	Rainfall in inches.	Chlorine per million.	Equivalent to NaCl per acre.
Mean of 12 summer periods to 1885	17·04	3·14	19·91
Mean of 12 winter periods to 1885–86	17·65	3·58	23·56
Average for 16 years (excluding winter 1872–73)	33·31	3·25	40·33
Average for 12 years to March, 1886	34·69	3·36	43·47

Lawes, Gilbert and Warington have found in the rain collected at Rothamsted, as a mean of six years monthly determinations, 1·99 of chlorine per million, with a mean rainfall of 33·15 inches, equivalent to 24·59 lbs. of common salt per acre. They found the amount of chlorides in the summer months to be less than one-half that of the winter months.

114. "Some Analogous Phosphates, Arsenates and Vanadates." By John A. Hall, Student in the Laboratory of Owens College.

The author describes a number of phosphates and arsenates corresponding to the vanadates previously described by H. Baker (*Trans.*, 1885, 353); the salts of which an account is given are the following:—

$Na_3AsO_4{\cdot}10H_2O$, Regular.
$Na_3VO_4{\cdot}7H_2O$
$Na_3PO_4{\cdot}7H_2O$
$Na_3AsO_4{\cdot}4\frac{1}{2}H_2O$.

115. "Agricultural Experiments with Iron Sulphate as a Manure during 1886." By A. B. Griffiths, Ph.D.

The author and others have grown various crops with iron sulphate. Mr. Barlow (Oak Lane Farm, Whitefield, Manchester) after treating a plot of land of $\frac{1}{8}$ acre with 14 lbs. $FeSO_4$, obtained 5287 lbs. of potatoes, while a similar plot without sulphate only yielded 4891 lbs. Mr. J. J. Hunter (Newcastle-upon-Tyne) states that he obtained a crop of turnips grown with $FeSO_4$ as good as a similar crop grown with guano and dissolved bones; he states "it will be far cheaper to use copperas." The author has tested the value of $FeSO_4$ as a manure for hay. Taking two plots of land of the same size, one manured with $FeSO_4$ gave 6962 lbs. of hay (dry) while the other not so manured gave only 3496 lbs. Mr. Barlow has found that iron sulphate is a good manure for onions. The author has grown mangel-wurzel crops with the ordinary artificial manures and top-dressing of nitrate of soda. Two plots were taken of the same size and treated alike as far as artificial manures, quantity of seed used, &c. One plot was dressed with $\frac{1}{2}$ cwt. $FeSO_4$ to the acre. This plot yielded 32 tons of roots; and the other plot (which was treated precisely in the same way, *minus* the $FeSO_4$) gave 26 tons of roots.

The author has grown for the third time bean crops. The land manured with $FeSO_4$ yielded 50 bushels of grain, while the other crop (not manured with $FeSO_4$) gave 30 bushels of grain. He also finds that iron sulphate is a good manure for palms and india-rubber trees. He recommends $\frac{1}{2}$ cwt. of $FeSO_4$ per acre as a top-dressing. The iron sulphate has proved to be an antiseptic agent of great value for parasitic micro-organisms. The paper shows that $FeSO_4$ is apparently a better manure (for certain crops at least) than kainite. With a top-dressing of $\frac{1}{2}$ cwt. of $FeSO_4$, the author obtained 9 tons potato tubers; and with 2 cwts. of kainite as a top-dressing only 6 tons of tubers. In all crops grows with $FeSO_4$, the albuminoids and soluble carbohydrates are increased. Concerning the ashes of the plants, it is found that when the iron manure has been used, the ferric and phosphoric oxides are increased, and the potash decreased, in the ashes of all crops.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Statistical Society. Catalogue of the Library and Index: London, 1884.

Descriptive Catalogues of a Collection of Economic Minerals of Canada in the Indian and Colonial Museum: London, 1886:
from Geol. Survey of Canada.

Annual Report of the Department of Mines, N.S.W., for the year 1885: Sydney 1886: from the Department.

Life and Labours of John Mercer: by E. A. Parnell: London, 1886. from the Author.

Notice sur les Instruments enregistreurs construits par R. Frères.

The Chemistry of the Farm: by R. Warington: 4th ed.: London, 1886: from the Author.

Report of the Board of Governors of the Public Library, Museum, and Art Gallery of South Australia: Adelaide, 1886:
from the Board.

Proceedings of the Birmingham Philosophical Society: Birmingham, 1885-1886: from the Society.

Results of Experiments at Rothamsted on the Growth of Barley: by J. H. Gilbert, F.R.S.: from the Author.

Method of Analysis of Commercial Fertilisers: Washington, 1886.
from C. Harrison.

Commercial Organic Analysis: by A. H. Allen: vol. ii; 2nd edition:
from the Author.

II. *By Purchase.*

Lectures on the Physiology of Plants: by G. H. Vines: Cambridge, 1886.

Food Grains of India: By A. H. Church: London, 1886.

Tables to Facilitate Chemical Calculations: by W. Dittmar: Glasgow, 1885.

RESEARCH FUND.

A meeting of the Research Fund Committee will be held in December. Fellows desiring grants are requested to make application before December 11th.

At the next meeting, on December 18th, the following Papers will be read :—

"Researches on the Constitution of 'Azo- and Diazo-derivatives.' I. Diazoamido-compounds." By R. Meldola, F.R.S., and F. W. Streatfeild.

"The Influence of Silicon on the Properties of Iron and Steel." By Thomas Turner.

HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY, ST. MARTIN'S LANE.

ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 30. Session 1886–87.

December 16th, 1886. Dr. Hugo Müller, F.R.S., President, in the Chair.

Messrs. A. Percy Hoskins and M. Hunter were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. William Henry Coates, Hedon House, 11, Archway Road, Highgate, N.; Thomas Cooksey, B.Sc., 284, Pentonville Road, N.; Hamilton Emmons, Mount Vernon Lodge, Leamington, U.S.A.; Herbert McKeon, 123, Lansdowne Place, Brighton; J. F. McArthur, Belgrave Crescent, Eccles; David Henry Nayel, 21, Tay Street, Dundee; Joseph de Carle Smith, Junr., Norwich; Lionel W. Stansell, 16, Hardy Street, Maidstone; D. A. Sutherland, Burntisland Oil Works, Burntisland, N.B.

The following were duly elected Fellows of the Society:—

Messrs. Horace Edward Brothers; Francis J. H. Coutts; Tamemasa Haga; Henry John Hardy; Michitada Kawakita; Walter Leach; Stephen James Pentecost; Henry Joshua Phillips; P. Yeshwant Sheshadri; Tetsukichi Shimidzu; Joseph Stapleton; William Phillips Thompson; Hikorokuro Yoshida.

The following papers were read:—

116. "Researches on the Constitution of 'Azo- and Diazo-derivatives.' I. Diazoamido-compounds." By R. Meldola, F.R.S., and F. W. Streatfeild.

In this paper the authors give the results of the application of the method described by them in a former communication (Trans., 1886, 624) to determine the constitution of the diazoamido-compounds. The

compound described in the previous paper, paradinitrodiazoamidobenzene, has the symmetrical formula $NO_2{}^{(1)}\cdot C_6H_4\cdot N_2{}^{(4)}\cdot NH\cdot C_6H_4{}^{(4)}\cdot NO_2{}^{(1)}$, and is consequently unsuited for the settlement of the question of intramolecular migration of the N_2-group. An unsymmetrical compound has therefore been prepared from paranitraniline and diazotised metanitraniline: it forms yellow needles melting at 211°, and furnishes on decomposition with chlorhydric acid a mixture of meta- and paranitranilines, and of meta- and paranitrochlorobenzenes. Its ethyl-derivative, prepared by the authors' method, melts at 148°, and gives on decomposition with chlorhydric acid a mixture of ethylmeta- and ethylparanitraniline, and of the two corresponding nitrochlorobenzenes. A method of identifying a mixture of meta- and paradiamines depending upon the colour reaction on oxidation ("indamine" formation) is described in the paper. In order to throw some light upon the reaction which takes place when these compounds are decomposed by being heated with chlorhydric acid, experiments have been made by heating diazonitrobenzene chlorides with chlorhydric acid in the presence of similar and dissimilar nitranilines, but the products were found to be identical in all cases with those of the corresponding diazoamido-compounds, so that it appears probable that these latter compounds are actually formed in the first instance. Metadinitrodiazoamidobenzene (Griess, *Liebig's Annalen*, **121**, 272) has been prepared by the action of 1 mol. proportion of $NaNO_2$ upon two of metanitraniline dissolved in chlorhydric acid; it forms straw-coloured needles melting at 194°, and decomposes when heated with strong chlorhydric acid into metanitrochlorobenzene and metanitraniline. The ethyl-derivative forms opaque whitish-yellow needles melting at 119°; it is decomposed by chlorhydric acid into ethylmetanitraniline and metanitrochlorobenzene. The formulæ of these compounds are $NO_2{}^{(1)}\cdot C_6H_4\cdot N_2{}^{(3)}\cdot NH\cdot C_6H_4{}^{(3)}\cdot NO_2{}^{(1)}$ and $NO_2{}^{(1)}\cdot C_6H_4\cdot N_2{}^{(3)}\cdot N(C_2H_5){}^{(3)}\cdot C_6H_4\cdot NO_2{}^{(1)}$. The next part of the paper deals with the question of the identity of mixed diazoamido-compounds. In accordance with the results obtained by Griess (*Ber.*, 1874, 1619) and other observers, it has been proved that the compound obtained by the action of diazotised paranitraniline upon metanitraniline is identical with the above-mentioned compound formed by the action of diazotised metanitraniline upon paranitraniline. The two compounds have the same melting point (211°), and give the same products on decomposition by chlorhydric acid; the same holds good with respect to their ethyl-derivatives (m. p. 148°). From these facts it follows that in the formation of this compound isomeric change must take place in one or the other mode of preparation, and in

order to throw light upon this question, the authors have prepared for comparison the ethyl-derivatives resulting from the action of the diazotised nitranilines upon the ethylnitranilines. Thus by combining diazotised metanitraniline with ethylparanitraniline, a compound of the formula $NO_2{}^{(1)}\cdot C_6H_4\cdot N_2{}^{(3)}\cdot N(C_2H_5)^{(4)}\cdot C_6H_4{}^{(1)}\cdot NO_2$ is obtained. This is *isomeric* with the ethyl-derivative (m. p. 148°) above described; it melts at 174—175°, and is decomposed by chlorhydric acid into metanitrochlorobenzene and ethylparanitraniline. On the other hand, by the action of diazotised paranitraniline upon ethylmetanitraniline, the compound $NO_2{}^{(1)}\cdot C_6H_4\cdot N_2{}^{(4)}\cdot N(C_2H_5)^{(3)}\cdot C_6H_4{}^{(1)}\cdot NO_2$ could not be obtained, but the product is apparently an amidoazo-compound forming orange-yellow needles melting at 187°. From diazotised paranitraniline and ethylparanitraniline, the compound $NO_2{}^{(1)}\cdot C_6H_4\cdot N_2{}^{(4)}\cdot N(C_2H_5)^{(4)}\cdot C_6H_4{}^{(1)}\cdot NO_2$ of m. p. 192°, described in a previous paper (Trans., 1886, 630), is obtained. In a similar manner, diazotised metanitraniline acts upon ethylmetanitraniline with the formation of the diazoethylamido-compound of m. p. 119°, described in the present paper.

The further applicability of the authors' method has been tested by preparing benzyl-derivatives of the foregoing dinitrodiazoamido-compounds. $NO_2{}^{(1)}\cdot C_6H_4\cdot N_2{}^{(4)}\cdot N(C_7H_7)^{(4)}\cdot C_6H_4{}^{(1)}\cdot NO_2$ crystallises from benzene in small yellow needles melting at 190°; the corresponding modification 1 : 3—3 : 1 melts at 142°, and the benzyl-derivative of the unsymmetrical dinitrodiazoamido-compound melts at 180°. The decomposition products of the benzyl-derivatives are analogous to those of the corresponding ethyl-derivatives. Summarising their results, the authors point out that the evidence obtained in the course of the present investigation shows a distinct tendency of the N_2-group to migrate to the para-position with respect to the other substituents: thus when metanitraniline is diazotised and combined with paranitraniline, the resulting compound has been proved to have the constitution $NO_2{}^{(1)}\cdot C_6H_4\cdot N_2{}^{(4)}\cdot NH^{(3)}\cdot C_6H_4{}^{(1)}\cdot NO_2$, and not, as might have been expected on first consideration, $NO_2{}^{(1)}\cdot C_6H_4\cdot N_2{}^{(3)}\cdot NH^{(4)}\cdot C_6H_4{}^{(1)}\cdot NO_2$. This migration is possibly effected through the formation of an intermediate additive compound as suggested by Victor Meyer (*Ber.*, 1881, 2447), but the authors propose to submit this point to further investigation.

Discussion.

Mr. Friswell asked did Professor Meldola invariably use the sealed tube method: might not a less violent method be employed? He thought that probably what had been said of the easy decomposability

of some of the amido-azo-compounds referred to might be extended to all such bodies.

Professor MELDOLA in reply, said that it was not always necessary to heat in a tube: mere boiling sufficed in many cases.

117. "The Influence of Silicon on the Properties of Iron and Steel." Part I. By Thomas Turner, Assoc. R.S.M.

After referring to the work of previous observers in this direction, including Bessemer, Gautier, Mräzek, Pourcel, Riley, Snelus, and others, the author gives an account of experiments undertaken to determine the influence of silicon on the purest form of iron obtainable in considerable quantities. For these experiments metal was taken from the basic Bessemer vessel, at the end of the blow, and before any addition of manganese had been made. This metal had the following composition: C = 0·03, Si = 0·0098, S = 0·039, Mn = 0·06, P = 0·04. It was mixed in a red-hot clay crucible with varying small quantities of silicon pig, containing 10·3 per cent. of silicon, the product being afterwards examined. The most important results are given in the following table:—

Si per cent. by analysis.	Limit of elasticity. Tons per sq. in.	Breaking load. Tons per sq. in.	Ratio limit to break.	Extension per cent. on 10 inches.	Reduction of area per cent.	Relative hardness.
0·0098	13·01	21·80	0·597	27·7	77·0	18
0·02	13·08	19·95	0·656	17·6	40·3	16
0·035	15·69	23·07	0·680	16·3	31·8	17
0·039	16·42	23·28	0·704	18·2	37·7	17
0·08	16·72	23·77	0·704	24·2	44·9	20
0·117	18·00	28·05	0·642	15·6	26·8	21
0·13	18·37	25·68	0·715	18·8	41·9	20
0·027	17·75	21·75	0·861	26·0	67·4	15

Other specimens were prepared to which more silicon was added, but these broke in pieces in attempting to roll them. The last specimen in the above list is not comparable with the others, as in this case the silicon existed in the *oxidised* condition, and the material more closely resembled the original metal in its behaviour.

The author draws the following conclusions from his experiments. That the addition of silicon, in the form of silicon pig, to the purest iron obtainable in commerce tends to distinctly reduce its suitability for being rolled. With only a few hundreths per cent. of silicon, the metal remains quiet in the mould. Red shortness appears to increase

with the amount of silicon, though the welding properties appear to be quite unaffected; the metal was tough when cold, with all proportions of silicon.

The limit of elasticity and tensile strength increase with addition of silicon, but the extension and the reduction of area are seriously diminished. The relative hardness is but slightly affected, and appears to be connected with the tenacity of the material.

With 0·4 of silicon and 0·21 of carbon a steel was obtained which was difficult to work hot, but could be hardened, and was very tough when cold. The author points out that these results would be considerably modified by the presence of larger quantities of carbon and manganese, such as are met with in practice.

Discussion.

In reply to a question by Dr. P. Frankland, Mr. Turner said that the high qualities of the sample which he had stated contained *oxidised* silicon (silica), were due not to the presence of this body, but to the absence of silicon.

The President asked if Mr. Turner could give any explanation of the boiling over, which he had referred to as occurring when the silicon-iron was added.

Mr. Turner said that the matter had been somewhat fully discussed elsewhere, and it was generally believed to be due to the evolution of gas which the iron had been able to retain in consequence of its containing silicon.

118. "The Distribution of Nitrifying Organisms in the Soil." By R. Warington, F.R.S.

The result of 69 experiments with clay or loamy soil from various depths shows that the nitrifying agent is present almost without exception down to 3 feet from the surface; samples from below this depth did not always exhibit the power of causing nitrification, and none of the samples of soil taken 8 feet from the surface produced nitrification. The nitrifying organism present in the subsoil is apparently in a feeble condition, nitrification starting much later in solutions seeded with subsoil than in those seeded with surface soil. Reasons are given for believing that in agriculture, nitrification is practically confined to the surface soil. The nitrogenous matter present in the subsoil is, however, nitrifiable if exposed to favourable conditions.

Discussion.

Dr. Percy Frankland remarked that it appeared desirable to use a nutritive material more constant in composition than urine in

experiments on nitrification. He objected to the term "nitrifying organisms:" Heræus, in Berlin, having recently proved that there were a considerable number of organisms capable of inducing nitrification.

Mr. Warington said that, however unfit urine might be for a certain class of experiments, as the object he had in view was to ascertain if nitrifying organisms were present, he maintained that it was sufficient to have an easily nitrifiable solution. The President had asked—were nitrifying organisms present in essentially siliceous soils? He had no experience except with Rothamsted soils, but he should say that they were if such soils were found to contain nitrates; moreover, Müntz had shown that if the organisms once became established in a bed, whatever its nature, it became more or less capable of effecting nitrification in suitable liquids passed through it.

119. "Isomeric Change in the Phenol Series. The Action of Bromine on the Dibromonitrophenols." By A. R. Ling.

The author's experiments have been conducted with the view of, if possible, obtaining some explanation of the isomeric change of dibrom*ortho*- into dibrom*oparanitro*phenol by the action of bromine first observed by Armstrong (*Chem. Soc. J.*, 1875, 520). As products of the action of bromine on dibrom*orthonitro*phenol he has obtained tetrabromoquinone, which is the chief product, together with *bromo*- and dibrom*oparanitro*phenol and orthobromodinitrophenol; dibromoparanitrophenol and bromine yielding *bromoparanitro*phenol, orthobromodinitrophenol and tetrabromoquinone.

It would seem that the formation of the bromanil involves the partial debromination of the dibromonitrophenol, the resulting brom*orthonitro*phenol then undergoing isomeric change: the bromoparanitrophenol thus produced is in part converted into bromodinitrophenol by the nitric acid resulting from the nitroxyl displaced in the formation of bromanil, and in part into dibromoparanitrophenol.

Discussion.

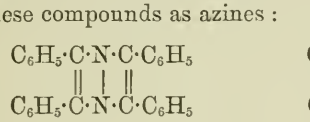
Mr. Groves asked if the author had tested his bromine for iodine; minute traces of this latter often had a most material influence: thus tribromophenol was readily converted into bromanil by means of bromine containing a little iodine, but not by pure bromine; and not a few other similar cases might be mentioned.

120. "Some Azines." By Francis R. Japp, F.R.S., and Cosmo Innes Burton, B.Sc.

The authors have endeavoured to ascertain whether ditolane-

azotide, $C_{28}H_{20}N_2$, and diphenanthrylene-azotide, $C_{28}H_{16}N_2$ (Trans., 1886, 826 and 843), belong to the class of the ketines or to that of the azines. They find that no ditolane-azotide is formed when benzil-monohydroxim is treated with tin and hydrochloric acid, contrary to what might be expected to occur if the azotide were a ketine.

They further show that there is a close analogy between diphenanthrylene-azotide and Witt's α-β-naphthazine (*Ber.*, **19**, 2794), and they have succeeded in synthesising the latter compound by heating β-naphthaquinone with ammonium acetate—a reaction which exactly corresponds with that in which diphenanthrylene-azotide is obtained from phenanthraquinone (Trans., 1886, 829, foot-note). These analogies, together with the fact that ditolane-azotide may be transformed into diphenanthrylene-azotide (Trans., 1886, 843), lead them to regard these compounds as azines :



SALE OF THE "ABSTRACTS OF PROCEEDINGS."

The "Abstracts of Proceedings" are purchasable at a price of seven shillings and sixpence per annum, post free. Intending subscribers are requested to apply to Mr. Van Voorst, Paterноster Row, London.

NOTICE TO AUTHORS OF PAPERS.

To facilitate the preparation of the abstract accounts of the Proceedings at the meetings of the Society, all authors are requested to furnish abstracts of their communications, and to send their papers so that they may be in the hands of the Secretaries, if possible, on the Monday before the day of meeting.

HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY, ST. MARTIN'S LANE.

ABSTRACTS OF THE PROCEEDINGS

OF

THE CHEMICAL SOCIETY.

Vol. III. Nos. 31—45.
JANUARY—DECEMBER, 1887.

EDITED BY THE SECRETARIES.

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DATES OF ISSUE OF THE MONTHLY NUMBERS OF THE JOURNAL OF THE CHEMICAL SOCIETY TO FELLOWS.

January number	was issued	3rd January.
February	,,	2nd February.
March	,,	4th March.
April	,,	1st April.
May	,,	4th May.
June	,,	3rd June.
July	,,	2nd July.
August	,,	5th August.
September	,,	1st September.
October	,,	8th October.
November	,,	4th November.
December	,,	3rd December.
Index	,,	will be issued early in January.

LIST OF GRANTS MADE FROM THE RESEARCH FUND DURING THE YEAR.

£25 to Professor E. H. Rennie: for the further study of the red colouring matter of *Drosera Whittakeri*.

£25 to Mr. Holland Crompton: for the study of the action of nitric acid on copper-zinc and copper-tin alloys with the object of determining whether the metals exist in combination or admixed.

£10 to Mr. C. H. Bothamley: for experiments on the use of dyes in photography, and especially on the sensitising action of the dye.

£25 to Mr. W. P. Wynne: for the determination of the nature of the products formed on oxidising nitric oxide by admixture with oxygen.

£10 to Mr. A. Wynter Blyth: for the study of the constitution of butter-fat.

LIST OF FELLOWS ELECTED DURING 1887.

Name.	Proposed.	Elected.
Barclay, Hugh	May 5th	June 16th.
Beasley, William C. T.	March 17th	April 21st.
Blundstone, Edwin R.	" "	" "
Bott, William	May 19th	June 16th.
Burford, Samuel F.	March 17th	April 21st.
Calder, Frank	November 3rd	December 1st.
Carrington, George, B.A.	June 16th	*November 17th.
Chenhall, James W.	March 3rd	April 21st.
Coates, William H.	December 16th, 1886.	February 3rd.
Cokesey, Thomas	" "	" "
Colman, Harold G.	February 17th	March 17th.
Colar, George	March 3rd	April 21st.
Crowther, Horace W.	November 3rd	December 1st.
Cribb, Cecil H.	February 3rd	March 3rd.
Cundall, James T.	February 17th	March 17th.
Dauber, Henry, Jun.	March 17th	April 21st.
Daniell, L. C.	April 7th	June 16th.
Dickson, Arthur	November 3rd	December 1st.
Dobbin, Leonard	January 20th	March 3rd.
Downes, Arthur H.	December 3rd, 1886	February 3rd.
Erhardt, Ernest F.	April 21st	June 16th.
Elborne, William	June 2nd	*November 17th.
Emmons, Hamilton	December 16th, 1886.	February 3rd.
Evans, Alfred J.	February 17th	March 17th.
Evans, William N.	May 19th	June 16th.
Fawsitt, Charles A.	November 3rd	December 1st.
Freeman, Frederic W.	April 7th	June 16th.
Galbraith, David R. S.	November 3rd	December 1st.
Geisler, Joseph F.	February 3rd	March 3rd.
Gordon, Hugh	March 3rd	April 21st.
Gover, Herbert J.	April 7th	June 16th.
Goyder, George A.	December 2nd, 1886	February 3rd.
Graville, Edward Day	April 7th	June 16th.
Gregory, William	March 17th	April 21st.
Green, John E.	May 5th	June 16th.
Hall, Edgar	January 20th	March 3rd.
Hall, Joseph C. A.	November 3rd	December 1st.
Harden, Arthur	February 17th	March 17th.
Hay, Alexander	January 20th	March 3rd.
Head, Casimir J.	November 3rd	December 1st.
Hedley, Thomas A.	February 3rd	March 3rd.
Heywood, James G.	November 3rd	December 1st.
Hogbin, Walter	" "	" "
Hori, E.	December 2nd, 1886	February 3rd.
Houlding, William	February 17th	March 17th.
Howard, David Lloyd	March 3rd	April 21st.

Name.	Proposed.	Elected.
Jackson, John S.	January 20th	March 3rd.
Jodhara, Khasberao	May 19th	June 16th.
Jones, Richard N.	April 7th	„ „
Kavanagh, J. M.	May 19th	„ „
Koga, Yoshimasa.	June 16th	*November 17th.
Lees, Samuel	November 3rd	December 1st.
Lennox, David.	„ „	„ „
Luttgen, Eberhard	„ „	„ „
Mackay, Angus	„ „	„ „
McArthur, J. F.	December 16th, 1886.	February 3rd.
McArthur, John	November 3rd	December 1st.
McGowan, George.	January 20th	March 3rd.
McKeow, Herbert.	December 16th, 1886.	February 3rd.
Marshall, William.	May 5th	June 16th.
Martineau, Sidney.	November 3rd	December 1st.
Matthews, William E.	„ „	„ „
McMinnes, Henry H.	April 21st	June 16th.
Miller, John A.	November 3rd	December 1st.
Mingaye, John C. H.	„ „	„ „
Moody, Gerald T.	February 3rd	March 3rd.
Nagel, David Henry.	December 16th, 1886.	February 3rd.
O'Connor, Joseph W.	February 3rd	March 3rd.
Ormiston, Archibald R.	November 3rd	December 1st.
O'Sullivan, Patrick T.	February 17th	March 17th.
Ostersetzer, Julius.	November 3rd.	December 1st.
Overend, Fred. L.	May 5th	June 16th.
Phillips, J. Stanley	„ „	„ „
Rawlins, Edward.	March 3rd.	April 21st.
Reay, Thos. Burden	December 2nd, 1886.	February 3rd.
Redwood, Theophilus H.	February 17th	March 17th.
Richardson, William H.	June 16th	*November 17th.
Richmond, Henry Droop	January 20th	March 3rd.
Robertson, George.	February 17th	March 17th.
Ruppel, Arthur H. F.	January 20th	March 3rd.
Schubart, Louis H.	March 3rd	April 21st.
Scrutton, W.	January 20th	March 3rd.
Sheard, John T.	May 19th	June 16th.
Simmons, Leonard O.	March 17th.	April 21st.
Snape, Henry Lloyd	January 20th	March 3rd.
Sohn, Charles E.	December 2nd, 1886.	February 3rd.
Spencer, Walter S.	May 5th	June 16th.
Stanley, Arthur	January 20th	March 3rd.
Stansell, Lionel W.	December 16th, 1886.	February 3rd.
Stanger, W. Harry	February 27th	March 17th.
Stedman, Chas. S.	May 5th	June 16th.
Stocks, Herbert B.	June 2nd	*November 17th.
Strangman, James Pim	December 2nd, 1886.	February 3rd.
Sulman, Henry L.	May 19th	June 16th.
Sutcliffe, Samuel	March 17th	April 21st.

Name.	Proposed.	Elected.
Sutherland, D. A.	December 16th, 1886.	February 3rd.
Takaminé, Jokichi	December 2nd, 1886.	February 3rd.
Taylor, Andrew W.	November 3rd	December 1st.
Traphagen, Frank	April 7th	June 16th.
Vargas, José Maria	November 3rd	December 1st.
Wallis, Henry Weston	January 20th	March 3rd.
Ward, John Septibo	November 3rd	December 1st.
Warrington, A. Walley	June 16th	*November 17th.
Watson, Fred. P.	May 19th	June 16th.
Winder, Bartlett W.	November 3rd	December 1st.
Young, John W.	April 21st	June 16th.

* The names of Fellows elected on November 17th were accidentally omitted from the Proceedings of that date.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 31. Session 1886–87.

January 20th, 1887. Dr. Hugo Müller, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. Leonard Dobbin, Ph.D., 4, Cobden Road, Edinburgh; Edgar Hall, Town House, Queenboro', Kent; Alexander Hay, 84, West Parade, Lincoln; John Steele Jackson, The College, Epsom; George McGowan, Bangor, North Wales; Henry Droop Richmond, Park Lane, Tottenham; Arthur H. F. Kuppel, 52, Parrock Street, Gravesend; Henry Lloyd Snape, B.Sc., The Technical School, Manchester; W. Scrutton, University College, London; Arthur Stanley, 38, Trebovir Road, Earl's Court, S.W.; Henry Weston Wallis, 7, Auckland Road, Clapham Junction, S.W.

The following papers were read:—

1. "Some Silicon Compounds and their Derivatives." By J. Emerson Reynolds, M.D., F.R.S.

Although large numbers of silicon analogues of carbon compounds are known, it is pointed out that we do not find among the former any well-defined representatives of cyanogen and its derivatives. The present investigation was commenced some years ago with the primary purpose of obtaining such compounds, if possible, and generally of examining reactions in which the silicon haloids—particularly the tetrabromide—and organic nitrogen compounds take part. In the course of the work a number of new bodies have been obtained, only a few of which can, however, be regarded as cyanogen-derivatives.

The author, in this the first paper of a series, describes the action of silicon tetrabromide on thiocarbamide, as the products obtained in this branch of the enquiry were exhibited at the conversazione of the Royal Society last June.

It is shown that silicon tetrabromide in benzene solution acts in a very remarkable manner with thiocarbamide, the latter affording a condensed amide with which the tetrabromide unites. Eight molecules of thiocarbamide combine with only one of silicon tetrabromide at the temperature of boiling benzene. Attempts to make this amide unite with a larger proportion of the bromide only lead to decomposition. The product is a thick liquid at a temperature 65° C., below the fusing point of pure thiocarbamide (140° C.), and becomes solid at ordinary temperatures. Solvents of the tetrabromide do not extract any from this product, nor is it dissolved by any liquid without decomposition.

When boiled with anhydrous alcohol it affords a monobromo-derivative of pentathiocarbamide, which is obtained from the alcoholic solution in beautiful groups of silky crystals. At the same time bromethyl-thiocarbamide and bromethyl-dithiocarbamide are obtained along with ethylic silicates.

Discussion.

In reply to Mr. Rideal, Professor Reynolds said that in preparing silicon tetrabromide, it was essential to use silica which had been precipitated in the gelatinous form and to mix it most intimately with the carbon (lampblack); the action of the bromine took place at an extremely high temperature. Replying to the President's question—Had analogous compounds been obtained from urea? he said that urea did react with silicon tetrabromide, but not in the same way as thiocarbamide.

Dr. Armstrong remarked that assuming the bromine to be the linking agent, it was noteworthy that in the silicon compound and also in that of ethyl bromide with thiocarbamide the ratio was $Br : 2CSN_2H_4$: this perhaps might be regarded as an indication that the thiocarbamide molecule had at least the formula $C_2S_2N_4H_8$; the ratio in the remarkable compound with bromine was, however, different.

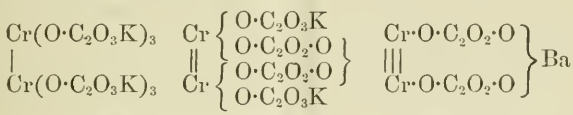
2. "Chromo-organic Acids. Part I. Certain Chromoxalates." By Emil A. Werner.

This paper contains an account of the salts resulting from the combination of chromium oxalate with certain metallic oxalates. A study of these compounds has led to the conclusion that they cannot be considered as ordinary double salts, but are in point of fact salts of complex chromoxalic acids. A similar view of the constitution of these compounds was advanced by Malaguti in 1843, but strange to say has been entirely ignored, since all workers with these particular compounds (with the exception of Clarke and Kebler) have treated them as

double or triple salts. Malaguti's view has been considerably extended, and new experimental evidence furnished in support of it; it has also been shown that the oxalic radicle can be displaced by those of other organic acids, salts of which have been obtained.

The paper concludes with the description of a new series of chromoxalates, whose members are shown to be closely related to those already known.

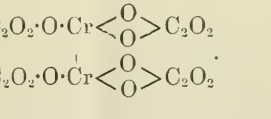
The following are examples of the formulæ given by the author to the three classes of salts:—



Blue salt. Red salt. Green salt.

Discussion.

Dr. Japp thought that some of the provisional constitutional formulæ proposed by the author for the various series of chromoxalates were open to criticism. In the formula for the salt of the "red series," for example, two oxygen-atoms, united to oxalic acid radicles, were represented as satisfying each other's affinities—an arrangement which would place these stable salts in the same category as the explosive peroxides of acetyl and benzoyl; whilst at the same time the two chromium-atoms in the formula were doubly linked. It was only necessary, however, to suppose that these vacant affinities of the chromium-atoms were satisfied by those of the oxygen-atoms in order to represent the salts as perfectly normal, thus:—



The constitution of the salts of the "green series" was still more anomalous, as in these the chromium was represented as existing in a less saturated state than that in which it occurs in the chromous compounds.

Mr. J. M. Thomson drew attention to the interesting dichroic properties of the chromoxalates, the dichroism being especially marked in the case of the calcium salt described by Professor Hartley. The difference in the extent to which they exhibit dichroism was very remarkable, as it distinctly decreased as the atomic weight of the metal forming the double chromoxalate increased, the dichroism of the potassio-baric chromoxalate being small compared with that of the potassio-calcic chromoxalate or the potassio-lithic chromoxalate.

Had the author observed the same diminution of dichroism with increase in molecular weight in the salts formed from the organic bases which were mentioned in the paper? With the object of further examining the optical properties of these compounds, the speaker had recently prepared double potassio-chromoxalates containing nickel and cobalt; these salts, however, presented no specially marked dichroic properties. They are also more soluble than the calcium or barium salts, and more difficult to crystallise.

Dr. Foster Morley said that the "red salt," as formulated, would be a chrom*ous* salt; spectrum analysis might be expected to throw light on the question whether it actually was a compound of this order. From observations recently made in the laboratory of the University College, it appeared that the difference between the blue and red chromoxalates was of the same nature as between the known blue and red chrom*ic* salts.

Dr. Armstrong, agreeing with the previous speakers, said that a chrom*ous* salt, such as the red salt was represented to be, ought, like all chromous salts, to be a powerful reducing agent: not a word was said in the paper to indicate that such was the case. The green salt, according to the formula given, would be still more oxidisable: it was inconceivable that such a salt should be formed in presence of alkali and air. He thought all three were chrom*ic* salts.

Professor Reynolds, by whom the paper was read, said in reply that differences in dichroic properties such as were referred to by Mr. Thomson had been noticed in the case of the salts of organic radicles. The author was studying the spectroscopic behaviour of the salts described.

3. "Note on the Constitution of the Double Chromic Oxalates." By W. N. Hartley, F.R.S.

Some years ago (*Proc. Roy. Soc.*, **21**, 499) the author described a remarkable dichroic salt, a potassio-calcium chromoxalate, and at the same time he prepared a large number of similar salts, the analyses of which were not completed in time for publication. These were potassio-chrome oxalates containing strontium, barium, lithium, and thallium. Excepting the lithium and calcium salts they did not possess any striking optical properties. They crystallised freely.

On account of the manner in which these salts were formed, for instance:—

a. By dissolving chromic hydrate in oxalic acid and adding the bases or their carbonates;

b. By preparing the red potassium chromic oxalate, $Cr'''KC_4O_8{\cdot}3H_2O$, and adding neutral potassium oxalate thereto;

also by reason of their reactions with calcium, strontium, and barium salts, he came to the conclusion that they were really derivatives of a distinct acid which might be termed chromoxalic acid, and the formula following would represent its constitution—$Cr'''O_3(C_2O_2{\cdot}OH)_3$.

The following reasons may be stated as affording grounds for this view:—

1. The chrominm is not precipitated by alkalies.

2. When alkali is added a soluble salt of the alkali is produced instead of a precipitate of chromic oxide or hydrate.

3. The carbonates of the alkalis give soluble salts of the alkalis and no precipitate.

4. The formula given is the only one which explains the formation of such salts as $K_3Cr'''{\cdot}3C_2O_4$.

5. The blue salts such as $K_3Cr'''{\cdot}3C_2O_4$ are *formed with greater facility* than the red salt $KCr'''{\cdot}2C_2O_4$.

6. The blue salts give none of the reactions which are characteristic of oxalates, such as precipitation with chlorides of calcium, barium, &c.

7. The blue salts can be formed from the red, and the potassio-calcium chromic oxalate can be made by boiling calcium oxalate with the red salt according to the equation

$$\left.\begin{matrix}K\\Cr'''\end{matrix}\right\}2(C_2O_4) + Ca''C_2O_4 = \left.\begin{matrix}KCa''\\Cr'''\end{matrix}\right\}3(C_2O_4).$$

4. "Remarks on recent Papers by A. Baeyer and J. Thomsen on 'The Constitution of Benzene.'" By Alex. K. Miller, Ph.D.

The author contends that most of Baeyer's arguments fail to carry much weight, since they are based on reactions which admittedly involve intramolecular changes. Such reactions might be used with equal force either in support of or against almost any formula, according to the way in which the isomeric change be assumed to take place. It is shown, for instance, how the conversion of dihydroxyterephthalic ether into succinosuccinic ether may be explained with the help of the prism formula as readily as with Kekulé's symbol. The author also points out a weak point in the argument which Baeyer brings forward against the prism formula. Finally it is pointed out that Baeyer's arguments in support of the existence of a double bond in benzene are founded upon data which may perhaps be used as an argument in favour, but certainly do not prove the existence, of a pair of double bonds.

With reference to Thomsen's octahedral symbol for benzene, it is stated that the advantages claimed for it, namely, that it is a perfectly symmetrical space representation which admits of three possible disubstitution-derivatives, and three only, are perfectly well founded.

It is, however, pointed out that the symbol differs in some important respects from Kekulé's symbol; it is impossible, for instance, to represent quinone as a diketone, the only representation possible being that in which each oxygen-atom is united by one affinity only to a carbon-atom; another difference is that Thomsen's symbol renders possible *four* disubstitution-derivatives of hexahydrobenzene. Finally, certain synthetical reactions such as the formation of succinosuccinic ether from succinic ether cannot well be represented with the aid of the symbol in question.

In conclusion, the author expresses the opinion that neither Baeyer's nor Thomsen's paper has contributed to the solution of the problem of the constitution of benzene.

At the next meeting, on February 3rd, there will be a ballot for the election of Fellows, and the following papers will be read:—

"An Explanation of the Laws which govern Substitution in the case of Benzenoid Compounds." By Dr. Armstrong.

"The Synthetical Formation of Closed Carbon chains."

Part I. "Some Derivatives of Tetramethylene." By Dr. W. H. Perkin, Junr., and H. Coleman.

Part II. "Some Derivatives of Pentamethylene." By Dr. W. H. Perkin, Junr.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 32. Session 1886-87.

February 3rd, 1887. Dr. Hugo Müller, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. Cecil Howard Cribb, 38, Soho Square; Joseph Frank Geisler, Mercantile Exchange Buildings, Hudson and Harrison Streets, New York; Thomas Albert Hedley, 41, St. Jean Baptiste Street, Montreal; Joseph William O'Connor, 28, Aberaeron Place, N.W.; Gerald Tattersal Moody, 229, Rye Hill, S.E.

The following were elected Fellows of the Society:—

Messrs. William Henry Coates, Thomas Cooksey, Arthur Henry Downes, M.D., Hamilton Emmons, George Arthur Goyder, E. Hori, Hubert McKeow, J. F. McArthur, David Henry Nagel, Thomas Burden Reay, Charles E. Sohn, Junr., Lionel W. Stansell, James Pim Strangman, D. A. Sutherland, Jokichi Takaminé.

The following papers were read:—

5. "The Absorption of Gases by Carbon." By Charles J. Baker.

A series of experiments are described in which carbon in the form of animal charcoal, previously heated *in vacuo*, was saturated with oxygen, both dry and moist, at a low temperature; the carbon thus treated, enclosed in a vacuous tube, was then heated for some time at 100°, and finally the absorbed gas was extracted and analysed.

Using moist oxygen, it was found that no gas was given off at 12° from the carbon which had been exposed for one hour at −15° in such an atmosphere; on heating the carbon thus treated at 100° during seven days, and then exhausting at this temperature, it gave

about seven times its volume of gas consisting of carbon dioxide. No carbon dioxide was produced on digesting carbon and water vapour for a similar period and then exhausting.

Using dry oxygen and proceeding similarly, no gas was given off from the charcoal at 100°; however, on raising the temperature to about 450°, gas was expelled, consisting mainly of carbon monoxide mixed with carbon dioxide. Dried carbon was then charged with dried carbon dioxide, and the gas was extracted by heating at about 450° as before; it consisted of carbon monoxide and dioxide, the proportion of the former being less the more carefully the carbon was dried. The author, therefore, concludes that the more carefully moisture is excluded, the less does the carbon burn in the carbon dioxide which it absorbs; and further that carbon is burned directly to carbon monoxide by absorbed oxygen.

Discussion.

Mr. F. J. M. Page asked whether the author had ascertained if the same carbon could be used repeatedly; that is to say, was it possible to burn away the whole of the carbon, or was the action confined to the surface.

Professor Odling, who had communicated the paper, said this had not been ascertained; he thought, however, it was probable that the carbon would become less and less absorptive, but that the action would continue in proportion as absorption took place.

6. "An Explanation of the Laws which govern Substitution in the case of Benzenoid Compounds." By Henry E. Armstrong.

Certain mono-derivatives of benzene, especially those containing a hydrocarbon radicle, one of the halogens, hydroxyl or amidogen yield a mixture of the para- and ortho-di-derivatives in proportions which vary both according to the nature of the compound dealt with and of the reagent, and the conditions under which the change is effected; and if produced at all, the meta-derivative is formed in but a small proportion. If, however, the radicle present in the mono-derivative be NO_2, COH, CO_2H, SO_3H, the meta-di-derivative appears invariably to be the chief product. Hitherto no explanation of this difference in the behaviour of the two series of mono-derivatives has even been suggested.

In seeking to arrive at an explanation it is necessary to form a clear conception of the manner in which "substitution" is effected. The author is of opinion that in the first instance an additive compound is formed; and he points out that Kekulé has long since

insisted in the plainest terms on this interpretation of those cases of change which are commonly spoken of as "double decompositions."

He is inclined to believe that the tendency of negative to attract and combine with negative elements—to which he has of late frequently directed attention—is the effective cause; and that the additive compound is formed from those mono-derivatives which obey the "para-ortho law" by the fixation of the reacting molecule upon the carbon-atom which carries the radicle: separation of water or halogen hydride ensuing thereon, the radicle of the reacting molecule assumes the place either of an ortho- or of a para-hydrogen atom. It is easy to understand the formation of the ortho-di-derivative, as the hydrogen-atom displaced is associated with a carbon-atom contiguous to that to which the reacting molecule attaches itself. The formation of the para-compound is attributed by the author to the tendency towards symmetry, so frequently evidenced in cases of isomeric change and in other ways by benzenoid compounds; and not to the existence of any direct connexion between carbon-atoms relatively in the para-position. The formation of meta-derivatives is believed by the author to result from the addition of the reacting molecule not to the carbon-atom of the benzene-ring but *to the radicle* which in the mono-derivative is attached to one of the carbon-atoms of the ring; he is, however, of opinion that in order to explain why the additive compound thus constituted yields a meta-di-derivative, it will be necessary to obtain further information regarding the "dynamics" of such changes.

Discussion.

Professor Odling observed that any attempt to solve the problem of the action of the commonly employed reagents, chlorine or bromine, nitric acid and sulphuric acid on one set of phenic mono-derivatives to produce under ordinary conditions mainly para-di-derivatives, and on another set of phenic mono-derivatives to produce mainly meta-di-derivatives, was entitled to a thoughtful and grateful consideration. But in his opinion a distinction should be drawn between the abstract cause of the result—as when Professor Armstrong attributed the habitual preferential formation of para-derivatives to the existence of a tendency to the formation of symmetric compounds, and the mechanism leading to the result—as when he represented the formation of ortho-derivatives as being an almost necessary consequence of the particular process by which he conceived the substitution to be effected. The former suggestion did not appear to help the matter forward very much; but the latter suggestion was at any rate in the nature of a real explanation: though, for himself, he was not prepared to admit the general principle that the previous combination of

reagents was an invariable and determining condition of their reaction. Under exposure to bright daylight, a mixture of equal volumes of chlorine and marsh-gas, for instance, reacted even with violence; and, in his opinion, while the evidence as to the fact of their previous combination was of the smallest, the evidence as to the previous combination being the determining condition of the reaction was none at all. Admitting, however, that in the case of phenic reactions a previous combination took place in the particular manner so ingeniously conceived by Professor Armstrong as favouring the production of ortho-compounds, the general question, exemplified in the special case of the nitro-bromo-derivatives, for instance, why, starting from the mono-bromo-derivative we should get mainly a para-di-derivative instead of an ortho-di-derivative, and why, starting from the mono-nitro-derivative we should get mainly a meta-di-derivative rather than either a para- or an ortho-di-derivative, still remained a problem, and one of very great interest, towards the solution of which Professor Armstrong had, at any rate, made a serious advance. It was clear that the nature of the product depended a good deal on the conditions of, and modes of effecting, the reaction.

He might here say that having regard to the usual modes of experimenting, he was accustomed to point out that where the pre-existing radicle was one of the typical radicles formulated as Cl, OH, NH_2, and CH_3, respectively, or some closely related radicle, the tendency was to the formation of 1—4 di-derivatives; and that where the pre-existing radicle was one of the acidic radicles formulated as NO_2, SO_3H, and CO_2H, or some allied radicle, the tendency was to the production of 1—3 di-derivatives. Having regard to the want of absolute concordance even in the writings of the present day, and to the extreme confusion in the writings of the last twenty years, as to the attribution of the prefixes para-, ortho- and meta-, he preferred to speak of the different sets of compounds as 1—4, and 1—2 and 1—3 derivatives respectively. At the same time the expression of the primary 1, in each case, was for the most part superfluous, and might be omitted with advantage; only, to avoid confusing the other numerals with multiples, it was preferable to denote them by means of the small Roman or italic figures used by doctors when writing their prescriptions, instead of by the usual Arabic figures. Thus while speaking of the two liquid dibromobenzenes, or as he preferred to call them dibromo-phenoenes, as one-two, and one-three dibromophenoene respectively, he was accustomed to write and formulate them as ij-dibromo-phenoene or ij-$C_6H_4Br_2$, and iij-dibromo-phenoene or iij-$C_6H_4Br_2$ respectively, the so printed names and formulæ being much shorter and clearer than those usually employed. These expressions, more-

over, stand in direct relation to the facts that ij-dibromo-phenoene gives origin to two tribromo-derivatives, and that iij-dibromo-phenoene gives origin to three tribromo-derivatives. As regards the expression of the 1—4 or crystalline dibromo-phenoene, he was accustomed to write and formulate it as jv-dibromo-phenoene, or jv-$C_6H_4Br_2$; but it might be very well expressed as j-dibromo-phenoene or j-$C_6H_4Br_2$, which would associate it with the fact of its giving origin to one tribromo-phenoene only.

Mr. Groves referred to the absorption of chlorine in large quantity by chloroform and carbon tetrachloride, and thought that facts such as these ought to be taken into account. He did not think that the tendency to form symmetrical di-derivatives was so universal as suggested by the author: the formation of resorcinol from benzene-*para*disulphonic acid was a case in point.

Dr. W. H. Perkin, Jun., thought that the production from hydrazobenzene, not only of benzidine but also of an isomer, was evidence against Dr. Armstrong's view as to the manner in which para-compounds were formed.

Dr. Armstrong, replying to Professor Odling's objection that the para-derivative was the chief product, and not the ortho- as should be the case according to his (Dr. Armstrong's) explanation of the manner in which substitution was effected, said that this was by no means always the case: in a recent investigation of the chlorotoluenes, for example, it had been shown that about twice as much ortho- as para-dichlorotoluene was formed. The proportions in which para- and ortho-derivatives were formed, appeared, however, to vary greatly, and to depend very much on the conditions obtaining at the time of change. He was of opinion that the behaviour of the paraffins afforded the strongest evidence in support of his view that addition preceded substitution: the affinity of the carbon-atoms being all but satisfied, especially in the lowest terms, substitution was effected but slowly in consequence of the small extent to which the chlorine was able to combine with the paraffin; and it was most important to observe that when chlorine had once become introduced, the introduction of other atoms could be effected more and more readily—the chlorine already introduced rendering the molecule more ready to combine with chlorine. Mr. Groves's reference to the solubility of chlorine in chloroform and carbon tetrachloride was most appesite. The behaviour of hydrazobenzene appeared to him to be perfectly in harmony with his views, the isomer formed together with benzidine being the ortho-compound. Cases such as were referred to by Mr. Groves were probably not simple isomeric changes, but involved the successive occurrence of several distinct changes.

7. "Some Derivatives of Tetramethylene." By G. H. Calman and Dr. W. H. Perkin, Jun.

On heating calcium tetramethylenemonocarboxylate with lime, a gas and an oil are produced, two-thirds of the former consisting of ethylene, and the remaining third being a mixture of hydrogen, methane and carbonic oxide.

The oil contains two new ketones, ditetramethylene ketone—

$$CH_2\left\{\begin{matrix}CH_2\\CH_2\end{matrix}\right\}CH\cdot CO\cdot CH\left\{\begin{matrix}CH_2\\CH_2\end{matrix}\right\}CH_2.\quad \text{B. p. } 204\text{—}205^\circ;$$

and methyltetramethylene ketone or acetyl-tetramethylene—

$$CH_3\cdot CO\cdot CH\left\{\begin{matrix}CH_2\\CH_2\end{matrix}\right\}CH_2.\quad \text{B. p. } 137\text{—}138^\circ.$$

Tetramethylene aldehyde has also been prepared by heating calcium tetramethylenemonocarboxylate with calcium formate; it boils at 115—117°.

8. "Derivatives of Pentamethylene." By Dr. W. H. Perkin, Jun.

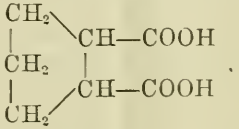
The sodium-derivative of ethyl malonate is converted by the action of trimethylene bromide into ethylic tetramethylenedicarboxylate and ethylic pentane-ω_2 ω_2-tetracarboxylate,

$$(COOEt)_2\cdot CH\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(COOEt)_2.$$

On hydrolysis this latter yields the tetracarboxylic acid. On heating this acid to 200° it is converted into α-pimelic acid and carbonic anhydride.

If ethylic pentanetetracarboxylate be treated with sodic ethylate, a disodium compound, $(COOEt)_2CNa\cdot CH_2\cdot CH_2\cdot CH_2\cdot CNa\cdot(COOEt)_2$, is formed. By treating this disodium-derivative with bromine, ethylic pentamethylenetetracarboxylate, $(COOEt)_2C\cdot CH_2\cdot CH_2\cdot CH_2\cdot C(COOEt)_2$, is obtained.

On hydrolysis this salt yields the tetracarboxylic acid, which on heating to 200° loses 2 molecules of carbonic anhydride, being converted into pentamethylenedicarboxylic acid—



a crystalline body melting at 160°.

Ethylic pentamethylenedicarboxylate is a disagreeably smelling oil, boiling at 249—252°.

Pentamethylenedicarboxylic anhydride melts at 64—67°.

Discussion.

Dr. A. K. Miller asked: Had Dr. Perkin made any attempts to prepare hexamethylene rings? Reactions which would furnish compounds so constituted might easily be suggested; and their production would afford considerable support to the arguments adduced in favour of the view that those now described were tetra- and penta-methylene ring-compounds.

Dr. Armstrong remarked on the peculiarly interesting and valuable character of Dr. Perkin's work on polymethylene-derivatives. In his paper on tetramethylene compounds Dr. Perkin had most clearly established the difference between what he called tetramethylene compounds and the *known* isomeric allyl-derivatives which it was conceivable might be formed in reactions such as were described; but it did not follow from this that the bodies in question were tetramethylene compounds: we were admittedly dealing with bodies of a novel type, and it was therefore necessary to be very cautious in applying knowledge gained by study of their physical properties, as we were unacquainted with the properties of any comparable series of compounds. Great differences were to be noted between maleic and fumaric acids, and between citra-, ita- and mesaconic acids, which could not at present be satisfactorily explained in terms of our conventional symbols; and it was conceivable that open-chain compounds might exist having properties very different from those of the known allyl-derivatives.

Dr. Perkin, Senr., said that in their physical properties the compounds discovered by his son were altogether peculiar: they behaved nearly as saturated bodies, and therefore the only way at present of representing them was to employ closed-chain formulæ. The maleic compounds behaved as unsaturated bodies, and the fumaric compounds were still further removed from saturated compounds. The properties of the tetramethylene compounds were in no sense akin to those of the maleic-fumaric, or citra-ita-mesaconic series.

Dr. Perkin, Junr., said that in the paper referred to he had only sought to prove that allylacetic and allylmalonic acids were different from what he had termed tetramethylene-mono- and di-carboxylic acids; the latter might have some quite different formulæ to those which he had proposed, but they could not be regarded as parallel compounds to the fumaric or itaconic acids.

Dr. Armstrong added that it must not be forgotten that trimethylene, $CH_2{\cdot}CH_2{\cdot}CH_2$, although unsaturated, behaves practically as a saturated compound.

9. "The Decomposition of Potassium Chlorate and Perchlorate by Heat." By Percy F. Frankland, Ph.D., B.Sc., A.R.S.M., and John Dingwall.

The authors have reinvestigated the points in the decomposition of these bodies which were raised by Teed (*Proceedings*, Nos. 12 and 16, 1885–86).

In the first series of experiments, potassium chlorate was partially decomposed by heating in a tube over a naked flame. The results are summarised in the following table:—

Percentage of oxygen evolved on weight of $KClO_3$ taken.	On $KClO_3$ actually decomposed.			
	Percentage of oxygen evolved.	KCl formed (per cent.).	$KClO_4$ formed (per cent.).	Proportion of oxygen evolved to 74·57 parts of KCl formed.
No. 1. 2·66	6·30	22·48	71·22	20·87
No. 2. 5·19	6·27	22·43	71·30	20·84
No. 3. 6·47	7·09	23·68	69·23	22·32
Equation—				
$10KClO_3 = 6KClO_4 + 4KCl + 3O_2$ requires	7·83	24·34	67·83	24·00
$8KClO_3 = 5KClO_4 + 3KCl + 2O_2$ requires	6·53	22·81	70·66	21·33
$2KClO_3 = KClO_4 + KCl + O_2$ requires	13·05	30·42	56·53	32·00

Percentage of oxygen evolved on weight of $KClO_3$ taken.	On $KClO_3$ actually decomposed.			
	Percentage of oxygen evolved.	KCl formed (per cent.).	$KClO_4$ formed (per cent.).	Proportion of oxygen evolved to 74·57 parts of KCl formed.
No. 1. 6·89	8·14	25·44	66·42	23·88
No. 2. 6·78	8·76	26·03	65·21	25·10
No. 3. ($KClO_3$ mixed with powdered glass) 14·30	15·34	33·55	51·11	34·10

In further experiments the potassium chlorate was decomposed at a temperature below that at which potassium perchlorate suffers change, by heating it in the vapour of boiling sulphur (p. 14).

It appears, therefore, that when potassium chlorate is partially decomposed by heat, the decomposition may be expressed by equations of the type $8KClO_3 = 2O_2 + KClO_4 + 3KCl$, and that the more complete the decomposition the more does it approximate to that indicated by the equation $2KClO_3 = KClO_4 + KCl + O_2$.

The authors have fully established the formation of potassium chlorate in the first stages of the decomposition of potassium perchlorate. This reaction is of interest as forming an exception to Berthelot's law of maximum work, the well-known formation of potassium perchlorate from potassium chlorate being a reversible change.

In a first series of experiments with perchlorate, the potassium chlorate was determined by means of the zinc-copper couple method. Finding, however, that the couple had a very slight action on perchlorates, a second series of experiments were made, in which the chlorate formed was determined by evaporation with chlorhydric acid; the results entirely substantiate those of the first series, and are as follows :—

Percentage of oxygen evolved on weight of $KClO_4$ taken.	On $KClO_4$ decomposed.			
	Oxygen evolved (per cent.).	KCl formed (per cent.).	$KClO_3$ formed (per cent.).	Oxygen evolved to 74·57 parts of KCl formed.
No. 1. 6·34	36·54	38·70	24·76	70·41
No. 2. 7·80	36·63	38·79	24·58	70·42
No. 3. 24·05	43·60	49·21	7·19	66·06
The equation— $7KClO_4 = 2KClO_3 + 5KCl + 11O_2$ requires	36·29	38·44	25·27	70·40

10. "The Action of Chlorine on Methyl Thiocyanate." By Dr. J. William James, University College, Cardiff.

The author describes the result of the action of chlorine on methyl thiocyanate, a reaction first studied by Cahours, and afterwards by Riche.

On passing dry chlorine into methyl thiocyanate at the ordinary temperature to complete saturation, the reaction being completed in sunlight, methyl thiocyanate is decomposed into *cyanuric chloride*, *thiocarbonyl chloride* ($CSCl_2$), and the *tetrachloride*, $CSCl_4$. The latter is identical with the perchlormethyl mercaptan of Rathke, obtained by the action of chlorine on carbon disulphide in presence of iodine. The chief reaction which takes place is : $3CH_3SCN + 11Cl_2 = C_3N_3Cl_3 + 2CSCl_4 + CSCl_2 + 9HCl$.

Cahours studied the reactions in a qualitative manner only; and Riche did not show the presence of either thiocarbonyl chloride or tetrachloride, and moreover, obtained a body of the formula C_2SCl_6, which, as is shown, must have been a mixture of $CSCl_4$ and $C_3N_3Cl_3$.

The author has further established that when chlorine is passed into thiocarbonyl chloride it is completely absorbed, forming thiocarbonyl tetrachloride; and that by the prolonged action of the gas this latter substance is decomposed into carbon tetrachloride and sulphur dichloride.

The well-known fact that carbon disulphide is converted by chlorine into these two bodies seems therefore to be the result of a series of reactions, viz.: (1) $CS_2 + 2Cl_2 = CSCl_2 + SCl_2$; (2) $CSCl_2 + Cl_2 = CSCl_4$; (3) $CSCl_4 + Cl_2 = CCl_4 + SCl_2$.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Old or New Chemistry: by Samuel E. Philips: London, 1886: from the Author.

Journal and Proceedings of the Royal Society of New South Wales: vol. xix: Sydney, 1886: from the Society

The Science of Agriculture: by F. J. Lloyd: London, 1884: from the Author.

Proceedings of the Illinois Pharmaceutical Association: Chicago, 1886: from the Association.

Myoporinous Plants of Australia: by F. v. Mueller: II. Lithograms: Melbourne: from Dr. Hugo Müller.

Memorias de la Sociedad Cientifica "Antonio Alzate": tomo I, num. 1: Mexico, 1886: from the Society.

A Treatise on Chemistry: by Sir H. E. Rocoe and C. Schorlemmer: vol. iii; part 2: London, 1886: from the Authors.

Transactions of the Sanitary Institute: vol. vii: London, 1886: from the Institute.

Norwegian North Sea Expedition. XVI. Zoology. Mollusca. II: by H. Friele: Christiania, 1886: from the Editorial Committee.

Proceedings and Transactions of the Royal Society of Canada: vol. iii, for the year 1885: Montreal, 1886: from the Society.

Progress of a Century; or, the Age of Iron and Steam: by E. Lawrence: London, 1886: from the Author.

A Catalogue of Scientific Periodicals (1665–1882): by H. Carrington Bolton: Washington, 1885: from the Smithsonian Institution.

Index to the Literature of Explosives. Part I: by C. E. Munroe: Baltimore, 1886: from the Author.

Der Chilisalpeter, seine Bedentung und Anwendung als Düngemittel: von A. Stutzer: Berlin, 1886: from Mr. Warington.

II. *By Purchase.*

Lehrbuch der Angewendeten Optik: von C. Gänge: Braunschweig, 1886.

Aus Pharmazeutischer Vorzeit in Bild und Wort: von H. Peters: Berlin, 1886.

Die Analyse der Milch: von E. Pfeiffer: Wiesbaden, 1886.

Mohr's Lehrbuch der Chemisch-analytischen Titrirmethode: Neu bearbeitet: von A. Classen: 8 Auf: Braunschweig, 1886.

Vierteljahreschrift der Chemie der Nahrüngs- und Genussmittel. I Heft, 1 and 2 (continued): Berlin, 1886.

Zeitschrift für Biologie: vols. i–vii.

The Gas Engineer's Chemical Mannal: by J. Alfred Wanklyn: London, 1886.

At the next meeting, on February 17th, the following papers will be read:—

"The Influence of Temperature on the Heat of Dissolution of Salts." By S. U. Pickering.

"Studies on the Laws of Substitution in the Naphthalene Series." Part III. By Dr. Armstrong and W. P. Wynne.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 33. Session 1886–87.

February 17th, 1887. Dr. Hugo Müller, F.R.S., President, in the Chair.

Messrs. E. Hori and Charles E. Sohn, Jun., were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Harold Govett Colman, Owens College, Manchester; James Tudor Cundall, Dale Side, Hampton Redland, Bristol; Alfred John Evans, B.A., Sheegorah House, Boyle, Ireland; Arthur Harden, Ashville, Upper Charlton Road, Manchester; William Houlding, Stanley House, Anfield, Liverpool; Theophilus Horne Redwood, 154, Ladbroke Grove Road, W.; George Robertson, Madeira Villa, Woodford, Essex; W. Harry Stanger, 23, Queen Anne's Gate; Patrick T. O'Sullivan, 57, Great Britain Street, Cork.

It was announced that the following changes in the Council List were proposed by the Council:—

As President: Mr. W. Crookes, F.R.S., vice Dr. Hugo Müller, F.R.S.

As Vice-Presidents: Professor McLeod, F.R.S., Professor Schorlemmer, F.R.S., and Mr. Ludwig Mond, vice Mr. Crookes, F.R.S., Professor Liveing, F.R.S., and Professor T. E. Thorpe, F.R.S.

As Ordinary Members of the Council: Professor A. H. Church, Dr. P. F. Frankland, Professor Kinch and Dr. H. F. Morley, vice Messrs. H. T. Brown, A. E. Fletcher, and Professors Meldola and Pickering.

Messrs. C. W. Heaton, P. F. Frankland and Wyndham Dunstan were appointed by the meeting to audit the Treasurer's accounts.

The following papers were read:—

11. "The Influence of Temperature on the Heat of Dissolution of Salts." By S. U. Pickering.

This is an extension of the author's previous work on the sulphates —entitled "The Influence of Temperature on the Heat of Chemical Combination" (Trans., 1886, 260)—which tended to show that the heat of dissolution of a salt does not increase regularly with a rise of temperature, but that irregularities occur at various points, so that the heat of dissolution must be represented by a series of curves. The experiments with potassium sulphate, hydrated and anhydrous magnesium sulphate and hydrated and anhydrous copper sulphate have been repeated, and the investigation extended to potassium, sodium, hydrated and anhydrous strontium chloride, potassium and the two strontium nitrates, the two sodium carbonates, sodium acetate and potassium sodium tartrate. The investigation comprises over 700 determinations, the mean results with each salt being deduced from two to five distinct series of experiments, each performed with different thermometers. The observations extended from 3° to 25°. In all cases it was found that the irregularities previously noticed were the result of error, and that the heat of dissolution of a salt is represented by a series of straight lines. In rising from low temperatures the heat of dissolution is expressed by a straight line up to a certain point, when the rate becomes suddenly lowered and remains constant till a further sudden reduction occurs at some still higher temperature. The average divergence of all the mean results from lines of perfect straightness amounted to less than one-thousandth of a degree.

With the normally anhydrous salts one lowering of the rate (amounting to about 30 per cent.) only was observed between 3° and 25°, occurring at temperatures between 14° and 9·5° in the various cases; while with the salts which combined with water of crystallisation the first alteration occurred at temperatures between 9° and 7°, and a second change took place at 21° to 18°; the frequency as well as the temperature of occurrence appearing to depend mainly on the tendency of the salt to combine with water. This lowering of the rate of increase in the heat of dissolution as the temperature rises must be accompanied by an increase in the specific heat of the solution which would indicate decomposition of some description.

Marignac's determinations of the specific heat of solutions give a rate of increase agreeing very closely with the author's results, and they also show that a further lowering takes place at temperatures above 25° up to 50°. Tilden's direct determinations of this rate at the higher temperatures show a very much larger decrease in the rate, but they cannot be freely accepted, as they are entirely at

variance, not only with all specific heat determinations, but also with a fundamental principle of thermochemistry.

The heat of combination of a salt with its water of crystallisation is deduced from the author's results. He concludes that it is not a constant quantity at all temperatures; the general effect of rise of temperature being to diminish it, although at very low temperatures this effect seems to be more than counterbalanced by some other cause, probably the tendency of the water molecules to unite with each other, the heat of combination diminishing then with fall of temperature. The more water a salt contains the more marked are both these results.

Discussion.

Dr. Alder Wright thought that the Society was to be congratulated on the fact that one of its members had undertaken the laborious and delicate work involved in making accurate thermochemical determinations of heats of dissolution, and in avoiding the numerous sources of error which attend such valuations. He found it somewhat difficult to realise the practicability of obtaining exactitude of such an order that the experimental errors should not exceed two or three calories, which apparently Professor Pickering claimed to have done. Julius Thomsen, in his most accurate and painstaking researches, generally found a minimum variation from the mean in consecutive observations of from $\pm$ 5 to $\pm$ 10 calories; and Dr. Alder Wright himself, whilst working on the heat of dilution of concentrated solutions (with, however, less complete appliances than those used by Thomsen), found that about $\pm$ 10 calories was the minimum experimental error attaching to each separate valuation. The question of the amount of the experimental error seriously affected Professor Pickering's conclusion that the curves indicating his results frequently consisted of two or more straight lines making an angle or sudden break in the curve; it would seem far more probable, *à priori*, and in view of the general course of physical phenomena, in which some value is a function of the temperature, that the curve is truly *a curve* throughout, expressible by some such symbols as $1 + \alpha t + \beta t^2$, where β may be + or —. Judging from some of Professor Pickering's diagrams, the deviations exhibited by some of his observations from the sets of straight lines deduced by him as mean results, are as great as, if not greater than, the deviations which they would exhibit from a mean curve of this kind; and until it had been shown that the deviations in this latter case were materially wider than could be accounted for by the degree of magnitude of the experimental errors, whilst in the former case this was not so (which so far Professor Pickering had not done), he should feel

some degree of difficulty in accepting the conclusion that the curves are not regular ones, but are portions of the bounding circumferences of irregular polygons.

[Professor TILDEN writes, with reference to the statement made by Mr. Pickering that he had used too little water in his experiments on the heat of dissolution of potassium sulphate, and that the salt could not have been all dissolved: that in every experiment of which the results were quoted in his paper the salt was entirely dissolved.]

12. "Periodates." By C. W. Kimmins, D.Sc., B.A. (Contribution No. IX from the Laboratory of Gonville and Caius College, Cambridge).

The author, at the suggestion of Mr. Pattison Muir, has re-examined certain periodates of potassium, silver and sodium, with the object of explaining the discordant results of various observers.

Besides the salt $Na_2H_3IO_6$, described by Langlois, he has obtained a sodium periodate of the formula $Na_3H_2IO_6$; he also describes a potassium periodate $K_3HI_2O_9$. He has prepared and analysed the following silver salts:—

Ag_2HIO_5, dark brown.	$AgIO_4$, bright yellow.
$Ag_2H_3IO_6$, dark red.	$Ag_4I_2O_9 \cdot 3OH_2$, light yellow.
$Ag_3H_2IO_6$, slate-coloured.	$Ag_4I_2O_9 \cdot OH_2$, claret-coloured.
$AgIO_4 \cdot OH_2$, orange.	$Ag_4I_2O_9$, chocolate-coloured.

13. "Sulphonic Acids derived from the β-Monohaloid-derivatives of Naphthalene." By Henry E. Armstrong and W. P. Wynne, B.Sc.

Experiment having shown that the sulphonic acids obtained from naphthalene under conditions by which the occurrence of secondary change—which undoubtedly takes place when sulphuric acid is used as a sulphonating agent—is avoided, differ from those formed by means of sulphuric acid; and that the α-monohaloid derivatives of naphthalene yield isomeric sulphonic acids: it became desirable to study the behaviour of the β-monohaloid derivatives.

By the action of fuming sulphuric acid at 130—140° on β-chloronaphthalene, Arnell (*Bull. Soc. Chim.*, **45**, 184) has obtained two isomeric acids: one of these yields a sulphochloride melting at 129°, which is converted into δ-dichloronaphthalene by distillation with PCl_5; the sulphochloride of the isomeride melts at 109° and yields ϵ-dichloronaphthalene.

By acting with SO_3HCl on β-chloronaphthalene in molecular proportions, the authors have also obtained two isomeric acids, which

are undoubtedly identical with those discovered by Arnell. The *barium* salt of the chief product, $(C_{10}H_6Cl{\cdot}SO_3)_2Ba{\cdot}4H_2O$, crystallises in laminæ; the *potassium* salt, $C_{10}H_6Cl{\cdot}SO_3K + H_2O$, crystallises in small scales. The isomeric salts, $(C_{10}H_6Cl{\cdot}SO_3)_2Ba$ and $C_{10}H_6Cl{\cdot}SO_3K{\cdot}\frac{1}{2}H_2O$, are much less soluble in water.

β-Bromonaphthalene, in like manner, yields two isomeric acids. The *barium* salt of the chief product, $[C_{10}H_6Br{\cdot}SO_3]_2Ba{\cdot}3\frac{1}{2}H_2O$, and the *potassium* salt, $C_{10}H_6Br{\cdot}SO_3K{\cdot}1\frac{1}{2}H_2O$, crystallise in thin octagonal scales. The corresponding salts of the isomeric acid are anhydrous and very sparingly soluble in water; the barium salt crystallises in tufts of flat needles, the potassium salt in thin lustrous laminæ.

β-Iodonaphthalene also yields two isomeric acids. The barium salt of the chief product, $[C_{10}H_6I{\cdot}SO_3]_2Ba{\cdot}4\frac{1}{2}H_2O$, and the potassium salt, $C_{10}H_6I{\cdot}SO_3K{\cdot}H_2O$, crystallise in thin hexagonal scales. The salts of the isomeric acid are very sparingly soluble in water: the lead salt, $[C_{10}H_6I{\cdot}SO_3]_2Pb{\cdot}2\frac{1}{2}H_2O$, crystallises in scales; the barium salt, $[C_{10}H_6I{\cdot}SO_3]_2Ba{\cdot}2H_2O$, in white flat needles; and the potassium salt, $C_{10}H_6I{\cdot}SO_3K{\cdot}H_2O$, in well-defined laminæ.

Inasmuch as the action takes place between theoretical quantities of the reacting bodies, there can be little doubt that the products result from primary changes: a very small proportion, however—at most 3 or 4 per cent.—of the haloïd compound, is converted into the acid yielding the less soluble salts. Assuming, as is probable, that the products from chloro-, bromo- and iodonaphthalene correspond in composition, the proof of the production of ϵ-di-derivatives in this manner is of considerable theoretical importance: although not absolutely placed beyond doubt, there is every reason to believe that ϵ-dichloronaphthalene is the *symmetrical heteronucleal* $\beta_2\beta_3'$-derivative; and the formation of such derivatives affords a clear indication of the existence of what one of the authors has termed a plane of symmetry in the naphthalene molecule, corresponding to a diagonal passing through two β-positions in the two nuclei of the naphthalene symbol, a more convincing proof of which perhaps is afforded by the complete conversion of β-naphthyl sulphate on heating at 100° into β-napthol-β-sulphonic acid, which is also an ϵ-di-derivative (*Ber.*, **15**, 203).

14. "The Decomposition of Potassium Chlorate and Perchlorate by Heat." By Frank L. Teed, D.Sc.

The results published in the paper on this subject by Dr. P. F. Frankland and Mr. J. Dingwall in No. 32 of these Proceedings, as far as they go, entirely confirm certain results obtained by me and announced in two papers, abstracts of which appeared in the "Proceedings" Nos. 12 and 16 of the Session 1885–86.

In my latter paper I say that when the salt is very gently heated, the decomposition more nearly approximates to the equation $22KClO_3 = 14KClO_4 + 8KCl + 5O_2$, to which Frankland and Dingwall make no reference, the majority of the results falling within the limits of this equation and of the equation $10KClO_3 = 6KClO_4 + 4KCl + 3O_2$. On adding these two equations together and reducing to the lowest terms, the Frankland-Dingwall equation is obtained, which is merely one of the many equations that could be formed to express intermediate stages of decomposition.

There seems to be an idea among certain chemists that the determination of the evolved oxygen and of the potassium chloride are insufficient data from which to construct an equation, and that it is necessary to directly determine the perchlorate formed; or at all events, the undecomposed chlorate. This idea is erroneous, because it is obvious that for every 74·5 parts of KCl formed there must have been 122·5 of $KClO_3$ decomposed; and of the resulting 48 parts of oxygen, what is not evolved in the free state *must* have gone to form perchlorate. Any determinations of the $KClO_3$ and $KClO_4$ are therefore unnecessary. To give the results in my second paper (the paper was not published and the data do not appear in the abstract).

No.	$KClO_3$ taken, grams.	Oxygen evolved, per cent.	KCl formed, per cent.	Amount of oxygen to 74·5 of KCl.
1	4·3782	3·60	11·58	23·16
2	6·865	1·27	4·73	20·00
3	9·291	1·61	6·00	19·99
4	4·759	1·60	6·14	19·41
5	4·4905	1·47	4·84	22·63
6	6·050	0·80	2·18	27·34

I heated more gently and carefully than Frankland and Dingwall, and so obtained a higher yield of perchlorate and less free oxygen than they appear to have done. The equation $22KClO_3 = 14KClO_4 + 8KCl + 5O_2$ demands 20 parts of oxygen to 74·5 of KCl.

I was very careful to point out in my former paper that no equation represents the decomposition of potassium chlorate, and only proposed the two I have submitted as marking the usual limits of the final products.

The results with perchlorate given in my second paper were:—

No.	$KClO_4$ taken, grams.	Oxygen lost, per cent.	KCl formed, per cent.	Amount of oxygen to 74·5 KCl.
1	2·4355	3·10	2·97	77·76
2	3·8825	4·47	4·41	75·59
3	1·850	7·30	7·82	69·55
4	1·217	35·21	40·33	65·04

Frankland and Dingwall have failed to notice the first high ratio of oxygen to KCl, by again driving off too much oxygen, and to this extent their results are incomplete.

It is obvious that perchlorate of potassium, when it loses more oxygen than expressed by the equation $KClO_4 = KCl + 2O_2$, must be forming a lower oxide of potassium chloride; and the only such oxide possible under the circumstances is the chlorate. Hence the necessity for determining the chlorate formed disappears.

Discussion.

Dr. Percy Frankland said that he regretted Dr. Teed was not present at the reading of his and Mr. Dingwall's paper, for he would then have clearly understood that they had in no way arrogated to themselves the originality of the experiments, which undoubtedly belonged to Dr. Teed. Their experiments had been made with the view of testing the correctness of Dr. Teed's results, and they had endeavoured to place these results beyond the possibility of doubt, not only by taking special precautions in the method of decomposing the salts, but also by actually determining the proportion of chlorate formed in the decomposition of perchlorate, and the proportion of perchlorate in the decomposition of chlorate.

15. "The Formation of Ethylic Cyanacetoacetate." By Dr. J. William James, University College, Cardiff.

If 50 grams (1 mol. proportion) of ethylic monochloracetoacetate be mixed with 40 grams (2 mol. proportions) of potassium cyanide, and 600 c.c. of 99½ per cent. alcohol, a reaction takes place slowly at the ordinary temperature, the product consisting of ethylic potassium cyanacetoacetate, $CH_2(CN)\cdot CO\cdot CHK\cdot COOEt$.

If an aqueous solution of this salt be acidified with dilute chlorhydric acid, *ethylic cyanacetoacetate* separates as a colourless oil, which solidifies, if cooled, to a mass of fine silky needles, melting at 26·5° C. It cannot be distilled under ordinary pressure.

Ethylic dichloracetoacetate and potassium cyanide interact under the same conditions in a totally different manner, forming *potassium dichloracetate* and ethylic acetate.

16. " The Relation of Diazobenzene Anilide to Amidoazobenzene." By R. J. Friswell and A. G. Green.

In a previous communication to the Society (Trans., 1885, 917) we have attempted to give a partial explanation of the manner in which the isomeric change of diazobenzene anilide into amidoazobenzene takes place. We have shown that, in all probability, previous to the conversion, a resolution of the molecule of the anilide into diazobenzene and aniline is brought about by the acid present, and that these bodies then reunite in a different manner to form amidoazobenzene.

Further than this we could not go, for it still appeared to us a mystery how it was possible that the anilide could be formed under conditions which ultimately lead to its resolution and recombination in a new form, for example, when 1 mol. proportion of HCl is present.

This last difficulty has been cleared away by the suggestions lately put forward by O. Wallach (*Annalen*, 235, 233), and the whole reaction now appears perfectly clear and straightforward. Diazobenzene combines with aniline *at once* when no excess of mineral acid is present to form diazobenzene anilide; the presence of free mineral acid, however, lessens the tendency to displacement of the amidogen hydrogen, and thus prevents (more or less completely according to the quantity of acid present) the formation of the anilide: under these conditions the tardier tendency to displacement of the para-hydrogen of the nucleus now comes into play and amidoazobenzene is *very slowly* formed. If only 1 mol. proportion of HCl is present, the anilide is formed, but not quantitatively, the acid though not sufficient to entirely counterbalance the tendency to displacement in the NH_2, yet keeps apart a certain quantity of the diazobenzene and aniline, which in course of time interact to form amidoazobenzene and are consequently removed. The conditions are thus altered, and equilibrium is again established by the resolution of a further quantity of the anilide, the constituents of which slowly combine as before to produce amidoazobenzene. In this way the whole of the anilide is slowly resolved and the products recombined to form the compound, which, although the most stable under the conditions, requires a considerable time for its production, thus allowing of the intermediate production of a more quickly formed but less stable body.

17. "Note on Wallach's Explanation of the Isomeric Transformation of Diazoamidobenzene into Amidoazobenzene." By R. Meldola, F.R.S.

In a recent paper published by Wallach (*Annalen*, **235**, 233), that author, who has contributed such valuable results to the chemistry of the azo- and diazo-compounds, puts forward an explanation of the transformation of diazoamido- into amidoazobenzene, which seems to me to call for some comment. I should have been unwilling to call in question any opinion emanating from such a well-known authority had it not been for the somewhat dogmatic statement,—that in the opinion of the writer the question now appeared to have received its final dismissal ("*ihre endgültige Erledigung*"). As such a statement is calculated to induce a feeling of false security on the part of those who have paid attention this most interesting case of isomeric change, I take the opportunity of putting upon record my own conviction that the explanation advanced does not materially contribute to the solution of the problem. According to Wallach's view the reason why amidoazobenzene is not formed as the first product is because the aniline upon which the diazo-salt acts is for the most part free, *i.e.*, its NH_2-group is not saturated, and the diazobenzene residue can therefore readily enter the group in place of one H-atom. But when the diazoamido-compound is in presence of excess of acid (or of easily decomposable salts) it becomes resolved into its constituents, and these then reunite in a different way, because the NH_2-group is saturated and the diazobenzene residue prefers entering the nucleus (in the para-position). The aniline *salt* is in this case, according to the author, in the same condition as a tertiary amine or a phenol. A little consideration will, however, show that the known facts will not bear this interpretation, for diazoamidobenzene is *always* the first product whenever diazobenzene chloride acts upon any mixture of aniline and aniline hydrochloride, and this shows a distinct preference for the amido-hydrogen of the free aniline to be first displaced. In the presence of aniline hydrochloride, on the view that the acid of this salt decomposes the diazoamido-compound into its constituents, we have therefore a mixture of diazobenzene chloride, aniline hydrochloride and free aniline; *i.e.*, the conditions are precisely the same as at the commencement of the experiment. Why under these reproduced conditions the diazobenzene chloride should now prefer attacking the para-H-atom of the aniline hydrochloride instead of the amido-H of the aniline, remains, after the proposed "explanation," as great a mystery as ever.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Calendar of the Pharmaceutical Society of Great Britain, 1887: from the Society.

Synoptic Tables of Chemistry: by A. E. Fourcroy: Translated by W. Nicholson: London, 1801: from J. Marshall, Esq., F.R.C.S.

List of Fellows, Members, Licentiates, and Extra-Licentiates of the Royal College of Physicians: London, 1887: from the Council.

Calendar of the Imperial University of Japan, 1886-87: Tokio, 1887: from the University.

Quantitative Chemical Analysis: by C. R. Fresenius: Translated by J. Lloyd Bullock: 5th ed.: London, 1859;

Laboratory Guide: by A. H. Church: 3rd ed.: London, 1874;

Sanitary Examination of Air, Water, and Food: by C. B. Fox: London, 1878;

Qualitative Chemical Analysis: by W. G. Valentin: Revised by W. R. Hodgkinson: 5th ed.: London, 1880:

from W. T. Bayne, Esq.

II. *By Purchase.*

Chemistry of the Sun: by J. Norman Lockyer: London, 1887.

L'Aluminium: Par H. St.-Claire Deville: Paris, 1859.

At the next meeting on March 3rd there will be a ballot for the election of Fellows, and the following papers will be read:—

"The Colouring Matter of Drosera Whittakeri." By Professor E. H. Rennie, D.Sc.

"Anhydracetonebenzil." By F. R. Japp, F.R.S., and Cosmo Innes Burton, B.Sc.

"Condensation of Benzil with Ketones." By the same.

"Constitution of Glycosine." By F. R. Japp, F.R.S., and E. Cleminshaw, M.A.

"Diphenylglyoxaline and its Homologues." By F. R. Japp, F.R.S.

"Dehydracetic Acid." By Dr. W. H. Perkin, Junr.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 34. Session 1886–87.

March 3rd, 1887. Dr. Hugo Müller, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. James Warne Chenhall, Churston, near Brixham, Devon; George Collar, B.A., 28, Sterndale Road, West Kensington Park, W.; Hugh Gordon, 3, Courtfield Gardens; David Lloyd Howard, Rectory Manor, Walthamstow; Edward Rawlins, Burley Road, Leeds; Louis H. Schubart, 201, West 125th Street, New York.

The following were elected Fellows of the Society :—

Messrs. Cecil Howard Cribb, Leonard Dobbin, Joseph F. Geisler, Edgar Hall, Alexander Hay, Thomas A. Hedley, John S. Jackson, George McGowan, Gerald T. Moody, Joseph W. O'Connor, Henry D. Richmond, Arthur H. F. Ruppel, W. Scrutton, Henry Lloyd Snape, B.Sc., Arthur Stanley, Henry Wallis.

The following papers were read :—

18. "Tartaric and Racemic Acids and the Magnetic Rotatory Power of their Ethyl Salts." By W. H. Perkin, Ph.D., F.R.S.

The author has very carefully determined and compared certain physical properties of the diethylic salts of ordinary tartaric and racemic acids, prepared by the usual method by saturating the alcoholic solution of the acid with hydrogen chloride. Both boil at 232—233° (corr.) under a pressure of 197 mm. They have the same relative density, viz. :—

Diethylic tartrate .. $d\frac{15^\circ}{15^\circ} = 1{\cdot}20972$ $d\frac{25^\circ}{25^\circ} = 1{\cdot}20189.$

,, racemate.. $d\frac{15^\circ}{15^\circ} = 1{\cdot}20983$ $d\frac{25^\circ}{25^\circ} = 1{\cdot}20214.$

They have also the same mean molecular magnetic rotatory power, viz. :—

Diethylic tartrate at 14·8° = 8·766
,, racemate at 15·5 = 8·759

It may therefore be concluded that the racemate is a mixture of the two tartrates.

Racemic is distinguished from tartaric acid by crystallising with 1 mol. proportion of water; the author finds that silver racemate, like the tartrate, is anhydrous. In preparing silver tartrate, he obtained an acid salt, $C_4H_5AgO_6{\cdot}H_2O$, crystallising in well-defined monoclinic prisms, measurements of which by Professor Haushofer are given. An acid silver racemate appears also to exist, but is much less soluble than the tartrate, and the crystals are small.

The relative densities of aqueous solutions of the two acids were determined, using (*a*) a solution containing 8·333 per cent., and (*b*) a solution containing 25 per cent., the latter being supersaturated in the case of racemic acid; the results are—

	(*a*.)	(*b*.)
Tartaric acid solution..	$d\frac{15^\circ}{15^\circ} = 1{\cdot}03703$	$d\frac{15{\cdot}3^\circ}{15^\circ} = 1{\cdot}12346.$
Racemic acid solution..	$d\frac{15^\circ}{15^\circ} = 1{\cdot}03712$	$d\frac{15{\cdot}3^\circ}{15^\circ} = 1{\cdot}12398.$

The relative densities of the solid acids were also determined :—

Racemic acid, $C_4H_6O_6{\cdot}H_2O$.. $d\frac{t^\circ}{4^\circ} = 1{\cdot}6873.$
,, ,, dehydrated ..... = 1·7782.
Tartaric acid ..... = 1·7594.

These results, the author considers, point to the conclusion that on dissolving in water racemic acid separates into the two tartaric acids, only a small quantity remaining unchanged. He is of opinion that the water is present in crystallised racemic acid as such; and he finds that if the hydrated acid be crystallised from absolute alcohol, well-defined anhydrous crystals are obtained much less soluble than tartaric acid in alcohol.

19. "Anhydracetonebenzil." By Francis R. Japp, F.R.S., and Cosmo Innes Burton, B.Sc.

Anhydracetonebenzil (formerly *dehydracetonebenzil*), $C_{17}H_{14}O_2$, was originally prepared by Japp and Miller (Trans., 1885, 27) by the

condensation of benzil with acetone under the influence of caustic potash; they concluded that it contained a closed chain formed by the interaction of the acetone with the lateral chain of the benzil. The authors adduce further evidence in support of this view.

Anhydracetonebenzil reacts with phenylhydrazine, forming the compound $C_{17}H_{14}O(N_2H{\cdot}C_6H_5)$ (slender, yellow needles, melting at 197°), which is not altered by heating with excess of phenylhydrazine.

By boiling anhydracetonebenzil for a few minutes with iodhydric acid it is deprived of an atom of oxygen, and yields a compound, $C_{17}H_{14}O$ (colourless prisms from alcohol; m. p. 110°). This reacts with phenylhydrazine, forming $C_{17}H_{14}(N_2H{\cdot}C_6H_5)$, which crystallises from alcohol in rosettes of short, yellow needles, melting with decomposition at 170—180°.

Fuming iodhydric acid and amorphous phosphorus at 130° convert anhydracetonebenzil into a hydrocarbon, $C_{17}H_{18}$, which crystallises from alcohol in colourless, long, flat needles, melting at 47°, and distilling under ordinary pressures with partial decomposition at 305° (uncorr.). The authors regard this hydrocarbon either as diphenylpentamethylene (1, 2), or as phenylbenzyltetramethylene (1, 1). It is not reduced to $C_{17}H_{20}$ by the action of the hydriodic acid at a higher temperature, as it would be if it were an unsaturated open-chain compound—diphenylamylene.

By reduction with tin and hydrochloric acid in alcoholic solution anhydracetonebenzil is converted into a compound, $C_{34}H_{34}O_2$, very sparingly soluble in alcohol, from which it crystallises in lustrous, minute rhomboidal plates, melting at 187—188°.

When boiled with sulphuric acid diluted with twice its volume of water, 2 mols. of anhydracetonebenzil part with 2 mols. of water, and unite, forming a compound, $C_{34}H_{24}O_2$, which crystallises from benzene in two forms—one with, the other without benzene of crystallisation. This substance melts with decomposition at 195—200°, evolving exactly one molecular proportion of carbonic oxide, according to the equation $C_{34}H_{24}O_2 = C_{33}H_{24}O + CO$. The compound $C_{33}H_{24}O$ crystallises from benzene in small plates of the formula $C_{33}H_{24}O,C_6H_6$, which, after expelling the benzene, melt at 162—163°. It reacts with phenylhydrazine, yielding $C_{33}H_{24}(N_2H{\cdot}C_6H_5)$ (pale-yellow, slender needles, very sparingly soluble in alcohol; m. p. 250°). In this respect it differs from its parent compound, $C_{34}H_{24}O_2$, which does not react with phenylhydrazine.

Anhydracetonebenzil, when treated with concentrated alcoholic chlorhydric acid in the cold, is converted into a compound, $C_{17}H_{13}ClO$, which crystallises from alcohol in flat needles with a silky lustre (m. p. 128°). When this compound is heated with alcoholic ammonia

at 100°, it yields the condensation product $C_{34}H_{24}O_2$ (m. p. 195—200°) already described.

When oxidised with dilute nitric acid, anhydracetonebenzil yields chiefly benzoic acid, together with paranitrobenzoic acid, oxalic acid, benzil, and a small quantity of a neutral nitrogenous substance crystallising in needles (m. p. 264°).

The authors have also commenced the study of the reactions of *anhydracetophenonebenzil*, $C_{22}H_{16}O_2$ (Japp and Miller, Trans., 1885, 36), which was not supposed by its discoverers to contain a closed lateral chain. This compound appears to react both with 1 and with 2 mols. of phenylhydrazine, but neither of the derivatives thus formed could be obtained free from the other. When boiled with fuming iodhydric acid, it is transformed like anhydracetonebenzil, parting with an atom of oxygen, and yielding a compound, $C_{22}H_{16}O$ (long flat prisms from alcohol; m. p. 92—93°). With alcoholic chlorhydric acid in the cold anhydracetophenonebenzil behaves like anhydracetonebenzil, forming a compound, $C_{22}H_{15}ClO$, which crystallises from alcohol in colourless, slender needles, melting at 115°.

20. "Condensation Compounds of Benzil with Ketones." By the same.

In order to ascertain whether the reaction in which anhydracetonebenzil and anhydracetophenonebenzil are formed (see foregoing note) is of general application, the authors have examined the action of benzil with various homologues of acetone. Caustic potash of sp. gr. 1·27 was used as the dehydrating agent. In every case 1 mol. of benzil was found to react with 1 mol. of the ketone, eliminating 1 mol. of water. The intermediate additive compounds, the formation of which was observed in the case of the reactions of benzil with acetone and acetophenone (Japp and Miller, Trans., 1885, 21 and 34), were not isolated.

The following compounds, which for purposes of nomenclature are *assumed* to be true homologues of anhydracetonebenzil, have been prepared:—

Methyl-anhydracetonebenzil, $C_{18}H_{16}O_2$. From methylethylketone and benzil. Colourless thin prisms from alcohol; m. p. 179°.

Dimethyl-anhydracetonebenzil, $C_{19}H_{18}O_2$. From diethylketone and benzil. Colourless rhomboidal plates from alcohol; m. p. 150°.

Ethyl-anhydracetonebenzil, $C_{19}H_{18}O_2$. From methylpropylketone and benzil. Colourless minute needles from alcohol; m. p. 156°.

Amyl-anhydracetonebenzil, $C_{22}H_{24}O_2$. From methylhexylketone and benzil. Tufts of colourless slender silky needles from alcohol; m. p. 150·5°.

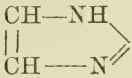
21. "Constitution of Glycosine." By Francis R. Japp, F.R.S., and E. Cleminshaw, M.A.

Debus showed (*Phil. Trans.*, **148**, 209) that glyoxal reacts with ammonia according to the two equations—

$$\text{I} \ldots\ldots \quad \underset{\text{Glyoxal.}}{3C_2H_2O_2} + 4NH_3 = \underset{\text{Glycosine.}}{N_4(C_2H_2)^{iv}_3} + 6H_2O.$$

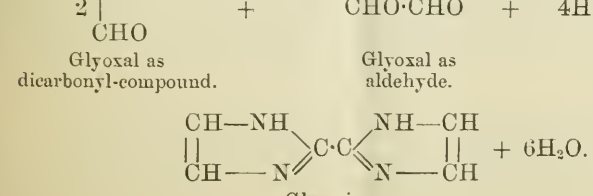
$$\text{II} \ldots\ldots \quad \underset{\text{Glyoxal.}}{2C_2H_2O_2} + 2NH_3 = \underset{\text{Glyoxaline.}}{C_3H_4N_2} + \underset{\substack{\text{Formic}\\\text{acid.}}}{CH_2O_2} + 2H_2O.$$

Radziszewski (*Ber.*, **15**, 1495) has suggested that the second of these reactions occurs in two stages. In the first stage, 1 mol. of glyoxal is hydrolysed, yielding formic aldehyde and formic acid; in the second, the formic aldehyde reacts with another mol. of glyoxal and 2 mols. of ammonia, forming glyoxaline. Interpreting this second stage by the light of the condensations of dicarbonyl-compounds with aldehydes and ammonia studied by one of the authors, glyoxaline would receive the formula


(Japp, Trans., 1883, 17).

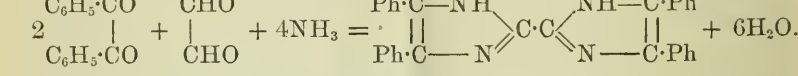
This formula is in keeping with the reactions of the compound and has found general acceptance.

It occurred to the authors that the second of the above reactions in which glycosine is formed, might in like manner be interpreted as belonging to the class of dicarbonyl-aldehyde-ammonia condensations, glyoxal being both a dicarbonyl-compound and an aldehyde. It would only be necessary to assume that, of the 3 mols. of glyoxal taking part in the reaction, one has the function exercised by the aldehyde in such condensations, whilst the other two act as dicarbonyl-compounds. On this assumption the reaction would occur according to Equation II (Trans., 1884, 672) of the general reactions of this class, save that in the present case, as the aldehyde is a dialdehyde, the molecular proportions of the other reacting substances are doubled :—



The glyoxal molecule of aldehyde function reappears as an oxalic acid residue in the formula of glycosine; the two glyoxal molecules of dicarbonyl function reappear in the form of two unsaturated groups —CH : CH— (comp. Trans., 1884, 673). In this respect the reaction would belong to the numerous class involving mutual oxidation and reduction between similar molecules, to which class the aldehydes furnish the largest contingent.

If the foregoing view is correct, it should be possible to substitute, in the foregoing reaction, for the two glyoxal molecules of dicarbonyl function, two diketone molecules containing the group CO·CO. Thus, by the action of ammonia on a mixture of benzil and glyoxal, a *tetraphenylglycosine* should be formed :—



This was found to be the case. Tetraphenylglycosine, prepared by the above method, crystallises from alcohol in long, very slender, silky needles, $C_{30}H_{22}N_4,C_2H_6O$, which readily part with their alcohol of crystallisation. It melts above 300°. It forms unstable salts.

Debus formulates glycosine as a tertiary amine on the quadruple ammonia-type (see reaction I). The formula above suggested differs from this in containing two imido-groups. In order to prove the presence of two displaceable hydrogen-atoms, the authors heated glycosine with benzyl chloride, and obtained *dibenzylglycosine*, $C_6H_4N_2(N{\cdot}C_7H_7)_2$, which crystallises from alcohol in oblique plates melting at 145°.

The authors have also prepared some new platinichlorides of glycosine. In addition to the diacid salt, $C_6H_6N_4,H_2PtCl_6$, described by Debus, they have obtained a *monacid salt*, $(C_6H_6N_4)_2H_2PtCl_6$, the existence of which was suspected by Debus, and a *tetracid salt*, $C_6H_6N_4(H_2PtCl_6)_2$, the latter being of the three that which is most readily prepared in a pure state.

A suggestion regarding the constitution of glycosine, similar to that here developed, has been thrown out by Wallach. He says (*Ber.*, **16**, 545, footnote) :—"Glycosine probably stands in the same relation to glyoxaline as dioxalethyline to oxalethyline." It is to be remarked, however, that dioxalethyline appears to be derived from an isomeride of glycosine, in which the two glyoxaline complexes are united at a different point.

22. "Diphenylglyoxaline and Methyldiphenylglyoxaline." By Francis R. Japp, F.R.S.

The author received from Mr. W. Palmer Wynne a small quantity

of a base, melting at 218°, obtained together with imabenzil, benzilimide, and benzilam by dissolving benzil in warm methylated spirit and saturating the solution with ammonia. This base remained in the last mother-liquors.

The author failed to obtain it on substituting pure alcohol for methylated spirit. An attempt was then made to prepare it, employing methylated spirit; but the only basic substance obtained was methyldiphenylglyoxaline (m. p. 235°), showing that the spirit contained aldehyde. An old specimen of wood spirit was then used. A new base was then obtained, which was deposited from alcohol in crystals not unlike those of Mr. Wynne's base, but melting at 227°. This proved to be *diphenylglyoxaline*, formed by the condensation of formaldehyde, contained in the wood spirit, with benzil and ammonia. The crystals differ in form according as they are deposited from hot or from cold alcohol—the latter form only resembling that of Mr. Wynne's base.

Analysis of Mr. Wynne's base gave figures intermediate between those required for diphenylglyoxaline and methylglyoxaline. A mixture of these compounds in molecular proportions was therefore allowed to crystallise from alcohol. The solution deposited crystals indistinguishable from those of Mr. Wynne's base, and, like these, melting at 218°. Finally, Mr. L. Fletcher has established the identity by crystallographical measurements. The hydrochlorides of the mixed bases also crystallise together in forms identical with those of the hydrochloride of Mr. Wynne's base.

23. "Dehydracetic Acid." By W. H. Perkin, Jun., Ph.D.

It is known that if dehydracetic acid, $C_8H_8O_4$, be treated with alkalis it is decomposed principally into acetic acid, carbonic anhydride and acetone, a small quantity of malonic acid also being formed.

The author finds, however, that in the first place dehydracetic acid is converted into two molecules of acetoacetic acid, $C_8H_8O_4 + 2H_2O = 2CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOH$. Dehydracetic acid reacts with phenylhydrazine and with hydroxylamine, forming the compounds $C_7H_8O_3(N_2H{\cdot}C_6H_5)$ and $C_7H_8O_3(N{\cdot}OH)$; and it therefore contains a carboxyl-group. The fourth oxygen-atom (not counting the carboxyl-group) is present neither as CO nor as OH, and the author therefore proposes the formula

$$\begin{array}{l} C{\cdot}CO{\cdot}CH{\cdot}COOH \\ \quad\| \qquad\| \\ CH_3{\cdot}C\cdot O\cdot C{\cdot}CH_3 \end{array} .$$

The action of aniline on methylic dehydracetate, in the author's opinion, is such as to prove the correctness of this expression, two

substances, *methylic phenyldimethylpyridine carboxylate* and *phenyldimethylpyridone*, being formed, which are both pyridine-derivatives, viz :—

$$\begin{array}{c} C\cdot CO\cdot C\cdot CO_2CH_3 \\ \| \quad\quad \| \\ CH_3\cdot C\cdot NPh\cdot C\cdot CH_3 \end{array} \qquad \text{and} \qquad \begin{array}{c} CH\cdot CO\cdot CH \\ \| \quad\quad \| \\ CH_3\cdot C\cdot NPh\cdot C\cdot CH_3 \end{array}.$$

An interesting synthetical proof of the correctness of the formula assigned to dehydracetic acid has lately been given by Conrad and Guthzeit (*Ber.*, **20**, 154).

24. "The Colouring Matter of *Drosera Whittakeri*." By Professor E. H. Rennie, M.A., D.Sc.

The author's attention was drawn to the presence of a red colouring matter in the tubers of the above-mentioned Drosera, which grows plentifully on the hills near Adelaide, South Australia, by Professor Tate. On inquiry he ascertained that Mr. Francis, of Adelaide, had extracted the colouring matter by means of carbon bisulphide, and had found that it was volatile, and that beautiful tints could be produced with it on silk by means of various mordants, but had not continued the investigation. To separate the colouring matter, the tubers were heated with hot strong alcohol. After distilling off the spirit, a little water was added and the precipitated colouring matter was then dried and sublimed; the product was a mixture of two substances differing in solubility in boiling alcohol and acetic acid. The less soluble was obtained in small brilliant red plates, canoe-shaped under the microscope, which melted at 192—193°. Analysis gave numbers fairly agreeing with those required by the formula $C_{11}H_8O_5$, which may represent a *trihydroxy-methylnaphthaquinone*. The reactions of the substance, in so far as they could be studied with the small quantity of material at disposal, serve to support the view that it is thus constituted. The second substance was finally obtained in needles, quite different in appearance from the red plates, though to the eye of much the same colour. Under the microscope single crystals seemed yellow, but wherever they overlapped the colour appeared deep orange to red. It fused at 164—165°. Analysis gave numbers fairly agreeing with the formula $C_{11}H_8O_4$.

25. "Further Notes on the Di-haloid Derivatives of Thiocarbamide." By George McGowan, Ph.D.

The author has succeeded in obtaining dithiocarbamide dibromide in beautiful large rhombic crystals, by the action of bromine on an

aqueous solution of thiocarbamide. At the ordinary temperature it is quite stable. By the further action of bromine on an aqueous solution, this dibromide is converted into carbamide, or, more probably, in the first instance into cyanamide, bromhydric and sulphuric acids being produced at the same time.

Sulphuretted hydrogen acts on dithiocarbamide dichloride, $(CSN_2H_4)_2Cl_2$, in alcoholic solution, producing thiocarbamide hydrochloride, $CSN_2H_4{\cdot}HCl$, and sulphur.

All attempts to prepare the dicyanide, $(CSN_2H_4CN)_2$, have failed. From the results of a number of experiments with different cyanides on thiocarbamide and its dichloride, the author concludes that probably the dicyanide is formed, but immediately breaks up, the separated sulphur being taken up by the excess of cyanide present and thiocyanate formed.

At the next meeting, on March 17th, there will be a Ballot for the Election of Fellows, and the following papers will be read:—

"The Action of Heat on Nitrogen Peroxide." By Dr. A. Richardson.

"The Formation of Naphthalenesulphonic Acid by means of Sulphuric Anhydride." By Dr. Armstrong and W. P. Wynne, B.Sc.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 35. Session 1886–87.

March 17th, 1887. Dr. Hugo Müller, F.R.S., President, in the Chair.

Messrs. Hugh Robert Mill, Gerald T. Moody and Arthur Stanley were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. William C. T. Beasley, Honiton School, Devon; Edwin Richardson Blundstone, B.A., 10, Wellington Mansions, Regent's Park, N.W.; Samuel Francis Burford, Halford Street, Leicester; Henry Danber, Kenmore, Waterloo Park, near Liverpool; William Gregory, Trent Valley Brewery, near Lichfield; T. O. Sandell, 1, Baron's Court Road; Leonard Owen Simmons, Fareham, Hants; Samuel Sutcliffe, Mostyn, North Wales.

The following were elected Fellows of the Society:—

Messrs. Harold G. Colman, James T. Cundall, Alfred J. Evans, Arthur Harden, William Houlding, Theophilus H. Redwood, George Robertson, W. H. Stanger, Patrick T. O'Sullivan.

The following papers were read:—

26. "The Action of Heat on Nitrogen Peroxide." By Dr. A. Richardson, University College, Bristol.

The dissociation of nitrogen peroxide has been investigated by Deville and Troost and other experimenters at temperatures between $-12°$ and $180°$; and it has been shown that while at low temperatures the molecule of the substance is represented by the formula N_2O_4, dissociation into nitrogen dioxide, NO_2, takes place with rise of temperature, being complete at $140°$.

Experiments have been made by the author to determine the change

which takes place at temperatures above 140°. On heating the peroxide at about 500°, the gas becomes nearly colourless, and is found to consist of nitric oxide and oxygen: the presence of the former being indicated by the formation of the dark blue liquid which results from the interaction of nitric oxide with nitrogen peroxide when the gas is condensed; and the presence of oxygen being demonstrated by the rekindling of a glowing match.

At a temperature at which decomposition is complete, the change would be represented by the equation $2NO_2 = 2NO + O_2$; the vapour-density of the dioxide being 0·23, that of the product is 15·3. On determining the density of the gas at temperatures between 130° and 500°, the numbers obtained were in agreement with the formula NO_2 at 140°, but as the temperature rose they more and more nearly approached that corresponding to complete dissociation. The curve representing the density of the gas at different temperatures shows that the decomposition of N_2O_4 into NO_2 is complete at 140°, and is immediately succeeded by the further dissociation of nitrogen dioxide into nitric oxide and oxygen. The form of the curve is that usually exhibited by dissociating substances, the change of density being most rapid at the temperature at which half the total number of molecules of the original substance are decomposed.

27. "Supersaturation of Salt Solutions." By W. W. J. Nicol, M.A., D.Sc.

This paper contains an account of experiments on the physical constants of supersaturated and dilute salt solutions. The solutions were examined in two ways: 1st, concentration constant and temperature varying; 2nd, temperature constant and concentration varying; in this way it was possible to pass from dilute to supersaturated solutions, and to examine the change in the various physical constants. The electric conductivity, specific viscosity and rate of expansion were examined by the first method. The specific viscosity and density by the second. In every case it was found that the curve corresponding to the non-saturated solutions was perfectly continuous with that for the supersaturated solutions. From this the author concludes that the constitution of dilute, saturated and supersaturated solutions is the same. Supersaturation is explained by the hypothesis that the substance in solution is not the same as that which crystallises out. A supersaturated solution of sodium thiosulphate deposited crystals of the composition $Na_2S_2O_3,H_2O$ when evaporated *in vacuo*, showing that the solution does not contain the pentahydrate. The author believes that the salt in solution is combined with the whole of the water, an opinion based on his experi-

ments on vapour-pressures and molecular volumes. Colour changes in solution are not, he believes, due to hydration, but to rearrangements of the salt molecule similar to that which occurs in the case of chromium sulphate.

Discussion.

Mr. Pickering said that he could not agree with Dr. Nicol in concluding that a supersaturated and non-supersaturated solution have identical constitutions, or that the salt was not combined with the solvent. A large number of the physical properties of solutions, such as the volumes of the dissolved salt, the lowering of the freezing point, &c., appear not only to afford no evidence of the existence of combination between the salt and the solvent, but would even, if taken alone, show that the radicles composing the salt itself are not combined; it was only by taking into consideration all the properties of solutions that we could obtain a correct conception of their nature. When examined from certain points of view, an ordinary and a supersaturated solution would, as Dr. Nicol shows, appear to be identical, but a study of the solubility of the salt leads to very different conclusions.

Referring to the nature of solution, Mr. Pickering said that chemists universally recognised two different forms or degrees of chemical combination, atomic and molecular, the latter being in some cases so weak that when examined from certain points of view only we could obtain no evidence of any combination at all; we should do well to consider the strong evidence which a study of minerals, alloys, isomorphous crystals, &c., afford of a form of combination less intimate even than that of our molecular compounds. The true molecules of solids and liquids, he considered, consisted in all probability of a large number of our formula molecules united together, and in the same way the true molecules of a solution would consist of aggregates of a large number of the molecules of the solvent with those of the salt, or of a definite molecular hydrate of the salt, according to circumstances, forming a unit of such complexity and instability that it would probably never exist entirely undissociated, and would therefore be affected in an apparently continuous manner by alterations in the physical conditions under which it existed (see *Chem. News*, **54**, 215).

Dr. Armstrong questioned the interpretation which Dr. Nicol had given of the continuous curves by which his observations were graphically expressed. It appeared to be established theoretically that a certain definite electromotive force, of more than a volt was required to electrolyse acidulated water; but actually any E.M.F., however

small, was found to suffice, the reason being apparently that owing to the presence of dissolved air action took place in a contrary direction; in like manner it was probable that in many cases in which dissociation was observed, if the effect of surfaces, &c., could be eliminated, the changes would be found to take place only suddenly, and would be represented by a broken, not by a continuous curve. The cases studied by Dr. Nicol were probably of the latter class, and if supersaturation took place gradually—part of the solution becoming supersaturated before even the whole was saturated, the curves representing the change in specific viscocity, &c., would necessarily be continuous. In discussing a problem such as that before the meeting, it was necessary to make a scientific use of the imagination and to consider the phenomena generally.

Dr. Nicol said that Professor Pickering's remarks more than ever convinced him that there was little or no difference in their views. Professor Pickering had abandoned the definite hydrate theory, and now believed in indefinite hydrate-aggregates of one molecule of salt and many hundred molecules of water. Where was the line to be drawn? He (Dr. Nicol) believed at the number of water molecules present in the solution; Professor Pickering stopped short of this, but where? As to the name to be applied to these aggregations, whether they should be called chemical or physical, he thought that according to the present use of the words the latter was the more appropriate. In reply to Professor Armstrong, Dr. Nicol pointed out that in an analogous case Wiedemann had found that the volume curve of hydrated salts exhibited irregularities long before their melting points were reached, and that this pointed to a rearrangement of the molecules similar to what would occur in supersaturated solutions were the hydrated salt present.

28. "The Formation of γ-Naphthalenesulphonic Acid by means of Sulphuric Anhydride and on γ-Dihydroxynaphthalene." By Henry E. Armstrong and W. P. Wynne, B.Sc.

By sulphonating naphthalene by means of sulphuric anhydride—both substances being intimately mixed with sand before admixture, and then vigorously shaken together—the authors have obtained a disulphonic acid which they believe is identical with that prepared by means of SO_3HCl (Proceedings, vol. ii, No. 27, p. 230). The sodium salt prepared from the product of the first experiment made at once crystallised in massive transparent diamond-shaped crystals of the oblique system; all attempts to prepare similar crystals from the product of the action of SO_3HCl have been unsuccessful, the salt rom this source being always obtained in characteristic thin plates; and

in a second experiment with SO_3 the sodium salt produced crystallised also in plates, distinct, however, in appearance, from those prepared from the SO_3HCl product, and this salt could not be caused to crystallise in the massive forms observed on the first occasion. Nevertheless it can scarcely be doubted that the acids prepared by the two methods are identical, as the sulphochloride from the SO_3 product has the same melting point (182°) as, and resembles in appearance, that from the SO_3HCl product, and both yield γ-dichloronaphthalene on treatment with PCl_5; the products of the action of bromine on the two sodium salts appear to be similar; and they behave alike on fusion with potassium hydroxide.

The dihydroxynaphthalene formed on fusing γ-naphthalenedisulphonic acid with potassium hydroxide would seem to be identical with that prepared by Clève by Griess's method from the amido-acid formed by reduction of 1 : 4′ nitronaphthalenesulphonic acid. It melts at about 250°; an alkaline solution on warming at once assumes a colour like that of a permanganate solution, but the colour rapidly changes to a dirty brown. The authors express the desire to reserve the right of further investigating this dihydroxynaphthalene.

29. "α-Cyanonaphthalenesulphonic Acid." By Henry E. Armstrong and S. Williamson.

It being ascertained that on sulphonating the α-haloid-derivatives of naphthalene the products are the 1 : 4 homonucleal sulpho-acid together with a small amount of a heteronucleal isomer, whereas on sulphonating α-nitronaphthalene and naphthalene-α-sulphonic acid the 1 : 4′ heteronucleal di-derivative is alone formed, it became desirable to study the behaviour of other α-derivatives of naphthalene containing negative radicles. α-Cyanonaphthalene was first sulphonated by means of SO_3HCl, but it was found advantageous to use fuming sulphuric acid instead; there appears to be only one sulphonic acid formed. The barium and potassium salts crystallise in different forms according to the conditions, and with different amounts of water; the most characteristic form of the barium salt is a hexhydrated modification, $[C_{10}H_6(CN)SO_3]_2Ba{\cdot}6H_2O$, which crystallises in long, thin, glistening plates; at low temperatures the potassium salt separates in transparent prisms, which probably belong to the oblique system, of the formula $C_{10}H_6(CN){\cdot}SO_3K{\cdot}3H_2O$. Both salts are dehydrated with difficulty. The sulphochloride, $C_{10}H_6(CN){\cdot}SO_2Cl$, crystallises from benzene in small glistening prisms. To judge from the result of a preliminary experiment with bromine, it is probable that the cyanosulphonic acid now described is a heteronucleal compound.

30. Addendum to Paper entitled "An Explanation of the Laws which govern Substitution in the case of Benzenoid Compounds." By Henry E. Armstrong.

In preparing the paper here referred to, having in mind the fact that the "basic" powers of nitrogen become enhanced by introduction of hydrocarbon radicles in place of hydrogen, it appeared to me not improbable that the behaviour of a compound such as dimethylaniline, for example, would not in all cases be strictly in accordance with the para-ortho-law; but I did not find any such departure recorded in the indexed literature. I have since become aware, however, that I failed to remember two recent papers, the one by A. Groll (*Ber.*, 1886, 198), the other by E. Nölting (*ibid.*, 545). According to Groll, dimethylaniline sulphate yields on nitration at a temperature not exceeding 5°, besides the paranitro-derivative, no less than 80—85 per cent. of *meta*nitrodimethylaniline; diethylaniline behaves similarly. Nölting not only confirms these statements, but adds that ethylaniline sulphate also yields a large proportion of meta-derivative; and that on nitrating ethylparatoluidine sulphate, the *meta*nitro-derivative, $NHEt : NO_2 : Me = 1 : 3 : 4$, is exclusively formed; whereas, according to Würster, the bromodimethylaniline obtained by brominating dimethylaniline dissolved in acetic acid is the *para*-modification; and, according to Beilstein and Kuhlberg, paracetoluide yields only the *ortho*nitro-derivative, $NHAc : NO_2 : CH_3 = 1 : 2 : 4$. These facts appear to materially strengthen my argument that the meta-derivatives are formed from an *additive* compound, resulting from the association of the reacting molecule with the radicle R′ of the parent compound.

In further support of the argument underlying my paper (Trans., 1887, 258) that the formation of an additive compound precedes that of the substitution derivative, I may take the opportunity to point out that on this assumption it is not difficult to understand that, for example, two hydrogen-atoms in ethylic acetoacetate, $Ac{\cdot}CH_2{\cdot}COOEt$, are not both immediately displaceable by sodium; probably an additive compound with sodium ethoxide is first formed, which becomes resolved into alcohol and acetosodacetate, $Ac{\cdot}CH_2{\cdot}CO_2Et + NaOEt = Ac{\cdot}CH_2{\cdot}(CO_2Et{\cdot}ONaEt) = Ac{\cdot}CHNa{\cdot}CO_2Et + EtOH$; owing to the influence which the sodium exercises on the contiguous CO_2Et group, this is no longer capable of uniting with sodium ethoxide, and only recovers the power of so doing on displacement of the sodium by a hydrocarbon radicle.

31. "The Transformation of Citric Acid into Pyridine-derivatives, and on the Constitution of Pyridine." By S. Ruhemann, Ph.D., Jacksonian Demonstrator in the University of Cambridge.

Hofmann and Behrmann have shown that citramide is converted by heating with sulphuric acid into citrazinic acid, the dihydroxypyridinecarboxylic acid in which both hydroxyls are in ortho-positions to the nitrogen-atom, the carboxyl being in the para-position. The author finds that the formation of the pyridine-derivative takes place even at ordinary temperatures if ethylic aceto-citrate be mixed with strong aqueous ammonia and the mixture allowed to stand several days; dilute chlorhydric acid then precipitates citrazinamide. The production of a pyridine-derivative in this manner is a strong argument, he thinks, in favour of Riedel's contention that the nitrogen-atom in pyridine is in connexion with the carbon-atom which relatively to it is in the para-position; and in further support of this view he states that no condensation takes place if methylamine be substituted for ammonia, there being in this case no available hydrogen-atom associated with the nitrogen-atom to separate with the hydroxyl and thus permit of the union of the nitrogen-atom with the para-carbon-atom. Incidentally it is mentioned as an indication of the mobility of the acetyl-gronp that if ethylic aceto-citrate be treated with phenyl hydrazine, the acetyl-derivative of the latter is formed; ethylic acetomalate and diacetotartrate behave similarly.

32. "Silver containing Bismuth." By William Gowland, A.R.S.M., Chemist and Assayer of the Imperial Mint, Osaka, Japan, and Yoshimasa Koga, Assistant Assayer.

An account is given of assays and metallurgical experiments made with the object of determining the effects produced by the presence of small quantities of bismuth on the ductility of silver, and on the uniformity of composition of silver bullion when in ingots of the form and size ordinarily met with in commerce. It is found: α. That when silver is obtained from copper containing bismuth by the liquation process with subsequent cupellation of the argentiferous lead, it contains part of the bismuth which was present in the copper; β. That this silver is brittle even when containing bismuth in but small amounts; γ. That ingots of such silver are not uniform in composition throughout their mass, the parts which have solidified last being richer in silver than the others; and δ. That when coinage bars of 900° millesimal fineness are prepared from it, they cannot be rolled without special treatment, and even then are hard and unsuitable for mintage.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Life and Works of Thomas Graham: by R. Angus Smith: edited by J. J. Coleman: Glasgow, 1884: from the Editor.

Natural Magick: by John Baptista Porta: London, 1658.

L'Art du Fabricant d'Étoffes en Laines: L'Art de préparer et d'imprimer les Étoffes en Laines: L'Art du Fabricant de Velours de Coton: par R. de la Platiere: Paris, 1780.

Prolusiones. ad Chemiam Saeculi decimi noni: by J. J. Winterl: Budæ, 1800: from the Royal Society.

New and Original Theories of the Great Physical Forces: by H. R. Rogers: London, 1878: from the Royal Society.

Die Milchprüfungs-methoden und die Controle der Milch in Städten: von P. Vieth: Bremen, 1879.

Easy Methods for the Examination of Milk: by P. Vieth: London, 1887: from the Author.

Geological and Natural History Survey of Canada: Annual Report and Maps: Vol. I (New Series), 1885: Montreal, 1886: from the Director.

New York Experimental Station: 5th Annual Report, 1886: Elmira, N.Y., 1887: from the Director.

II. *By Purchase.*

Zeitschrift für Physikalische Chemie, Stöchiometrie und Verwandtschaftslehre: Herausgegeben von W. Ostwald und J. H. van't Hoff: Band I, 1887 (*continued*): Leipzig.

The Anniversary Meeting will take place on March 30th, at 8 P.M.

At the next Ordinary Meeting, on April 7th, the following paper will be read:—

"Researches on the Constitution of Azo- and Diazo-derivatives. Diazo-amido-compounds." Part II. By R. Meldola, F.R.S., and F. W. Streatfeild.

HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY, ST. MARTIN'S LANE.

ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 36. Session 1887–88.

March 30th, 1887. Annual General Meeting. Dr. Hugo Müller, F.R.S., President, in the Chair.

The President delivered an address, of which the following is an abstract:—

The number of Fellows of the Society is 1508, of whom 30 are honorary foreign members. One foreign member, Professor A. Butlerow, has died during the year; and the Society has lost 12 Fellows by death:—Robert Alexander; Dr. James Apjohn, F.R.S.; Prof. F. S. Barff; Richard Cowper; M. G. Crossman; H. Sugden Evans; Rev. W. Flett; George Hirst; Dr. A. P. Price; J. A. Phillips, F.R.S.; E. R. Southby; and H. H. Watson.

20 Fellows have withdrawn:—W. E. Benton; T. F. Best; L. M. Deane; A. F. Dimmock: H. W. Field; W. J. Fuller; A. E. Garrod; Norman Graham; Thos. Harrison; Thos. Jamieson; Herbert Jones; Paul Mathews; P. B. Mills; J. D. McCarthy; Dr. A. P. Page; Dr. Robert Smith; G. Tunbridge; James Steel; A. H. Scott White; Philip Wright; and Wm. Cort Wright.

28 Fellows have been removed on account of arrears:—F. H. T. Allan; P. S. Brown; Robert Blair; Henry Child; G. Crampton; John Dale; Dr. Arthur Gamgee; A. M. Graham; G. Jarmain; R. H. Jude; F. Jordan; Wm. Marriott; J. E. Mayall; J. D. Mucklow; Dr. C. S. Marsden; John McCarthy; A. A. Nesbit; F. J. O'Farrell; Alfred Payne; A. W. Postans; J. E. H. Richardson; F. I. Scard; J. Steiner; K. Takemura; G. Valentine; Stephen Williams; and James Wilson.

110 new Fellows have been elected during the year.

The number of Papers communicated to the Society since the last anniversary meeting is the largest on record, being 118, or 5 in excess of the number read in 1880–81, and 14 in excess of the number read

last year. The President expresses the opinion that the Society has every reason to be satisfied with the share which it has contributed to the general progress of chemical science, adding that as we contemplate the ceaseless activity in chemical research now manifested all over the world, and which from year to year is continually on the increase, we are, nevertheless, bound to recognise the fact that vast as the work thus accumulated may appear, there remains still much to be accomplished. The more the field is worked the richer will be the harvest.

The number of Abstracts and Papers published in the Journal during the past five years are given in the following table:—

	1882.	1883.	1884.	1885.	1886.
General and Physical Chemistry..	219	205	237	331	235
Inorganic Chemistry.....	188	189	189	191	223
Mineralogical Chemistry	135	204	192	201	223
Organic Chemistry	837	739	939	1047	1056
Physiological Chemistry	112	73	118	142	100
Chemistry of Vegetable Physiology and Agriculture	270	163	324	218	160
Analytical Chemistry	284	195	256	337	289
Technical Chemistry.....	228	212	286	280	66
Total	2273	1980	2541	2747	2352
Papers in Transactions.....	65.	63.	57.	85.	85.

After dwelling on the importance of the determination of physical properties, the President gave a brief review of the more noteworthy chemical investigations of the year; and reference was then made to the work of the City and Guilds of London Institute for the advancement of technical education, with which the President of the Chemical Society is *ex officio* associated. Dr. Müller concluded his address with the following statement:—

The mistaken notion is still too prevalent that technical education has to confine itself to the theoretical considerations of known technical processes, and that a more extended acquisition of scientific knowledge is not required. It is obvious that a pupil educated on these lines may find by the time he is able to enter on his practical career that the processes with which he has been made acquainted have in the meanwhile become obsolete, and unless his education has been sufficiently comprehensive to enable him to strike out new lines for himself, he will be ill fitted to compete with those who have been educated on a wider basis.

Essential as it is to impart scientific knowledge to the future

manager, it is above all necessary to train him by practical work and research in the laboratory how to investigate a subject which may present itself in his daily occupation, whether it be some unexpected development in a new direction, or whether it be some new difficulty which confronts him in carrying out the processes under his direction. It is self-evident that such knowledge and such practical experience in carrying out investigations is not to be attained by merely attending one or two courses in the lecture room or in the laboratory. Those who mean to effectually qualify themselves for such functions can only accomplish this object by devoting years of patient and intelligent work under the guidance of the professor in properly appointed laboratories.

Prof. Odling proposed that the thanks of the meeting be given to the President for his address, and that he be requested to allow it to be printed. This motion was seconded by Dr. Gladstone, and accepted with acclamation by the Fellows present; the President acknowledged the compliment.

Professor Ramsay moved that thanks for their important services be given to the Editor, Sub-editor, Abstractors, and Librarian; the motion was supported by Mr. Dunstan. Mr. Groves replied.

Dr. A. K. Miller and Dr. Rideal were then appointed scrutators, and a ballot having been taken, the following were declared elected as Officers and Council for the ensuing year:—

President: W. Crookes, F.R.S.

Vice-Presidents who have filled the office of President: Sir F. A. Abel, C.B., D.C.L., F.R.S.; Warren De La Rue, D.C.L., F.R.S.; E. Frankland, D.C.L., F.R.S.; J. H. Gilbert, Ph.D., F.R.S.; J. H. Gladstone, Ph.D., F.R.S.; A. W. Hofmann, D.C.L., F.R.S.; H. Müller, Ph.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, Ph.D., F.R.S.; Sir Lyon Playfair, Ph.D., K.C.B., F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents: J. Dewar, M.A., F.R.S.; David Howard; H. McLeod, F.R.S.; Ludwig Mond; C. Schorlemmer, Ph.D., F.R.S.; W. A. Tilden, D.Sc., F.R.S.

Secretaries: H. E. Armstrong, Ph.D., F.R.S.; J. Millar Thomson, F.R.S.E.

Foreign Secretary: F. R. Japp, M.A., Ph.D., F.R.S.

Treasurer: W. J. Russell, Ph.D., F.R.S.

Ordinary Members of Council: Messrs. T. Carnelley, D.Sc.; M. Carteighe; A. H. Church; Frank Clowes, D.Sc.; P. F. Frankland, Ph.D.; R. J. Friswell; E. Kinch; R. Messel, Ph.D.; H. F. Morley, M.A.; J A. R. Newlands; W. Ramsay, Ph.D.; Thomas Stevenson, M.D.

The Treasurer, Dr. Russell, gave an account of the Society's financial condition. The receipts by admission fees and subscriptions had

been £2999 2*s.*; by sale of Journal, £369 19*s.* 2*d.*; by dividends on invested capital, £305 0*s.* 9*d.* The expenses on account of the Journal had been £2026 16*s.* 9*d.*; on account of the Abstracts of Proceedings, £163 4*s.* 11*d.*: on account of the Library, £323 11*s.* 10*d.*; on account of the Catalogue, £249; the total expenses being £3416 14*s.* 2*d.*; £500 had been invested in Metropolitan Board of Works 3½ per cent. stock, and there was a balance in hand of £1301 10*s.* 3*d.*

Mr. David Howard moved that the thanks of the Society be tendered to the Treasurer for his services during the past year; Mr. Friswell seconded the motion. The Treasurer in the course of his reply took occasion to point out that the expenses connected with the issue of the circular relating to the Imperial Institute and the collection of contributions thereto would not be borne by the Society, and that his connexion with the fund was a purely private one.

Mr. J. Spiller proposed a vote of thanks to the Auditors, which was seconded by Dr. H. F. Morley, and acknowledged by Mr. Wyndham Dunstan.

A vote of thanks to the Officers, Council, and Committee, was proposed by Mr. Warington, seconded by Mr. Davies, and acknowledged by Dr. Armstrong.

April 7th, 1887. Mr. William Crookes, F.R.S., President, in the Chair.

Mr. A. H. F. Ruppel was admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. L. C. Daniell, The Brewery, West Bergholt, near Colchester; Frederick William Freeman, Melbourne House, St. Albans; Herbert James Gover, 28, Broad Street, Hanley, Staffordshire; Edward Day Gravill, 106, Loughboro' Park, Brixton, S.W.; Richard Nelson Jones, L.R.C.P., Swansea Hospital, Swansea; Leonard James Reade, 12, Larches Lane, Wolverhampton; Frank Traphagen, Ph.D., Staunton, Va.

The following Papers were read:—

33. "Researches on the Constitution of Azo- and Diazo-derivatives. II. Diazoamido-compounds (continued)." By R. Meldola, F.R.S., and F. W. Streatfeild.

The authors describe the results of their experiments on the decomposition of the dinitrodiazoamido-compounds and their ethyl-deriva-

tives by cold chlorhydric acid. By a method described in the paper the products can be isolated and identified without the application of heat at any stage. The results show that the decomposition by cold acid takes place in the same manner as with hot acid, the most noteworthy instance being that of the unsymmetrical compound of m. p. 211° and its ethyl-derivative of m. p. 148°, both of which yield the same *mixed products* as when hot acid is employed. Thus the former compound yields *m*- and *p*-nitrodiazobenzene chlorides and *m*- and *p*-nitraniline, and the latter yields the same diazobenzene chlorides, together with the two corresponding ethylnitranilines. The two ethyl-derivatives prepared respectively by the action of diazotised *p*-nitraniline upon ethyl-*m*-nitraniline (m. p. 187°) and of diazotised *m*-nitraniline upon ethyl-*p*-nitraniline (m. p. 174—175°) behave in an analogous manner when decomposed by cold acid, the first giving *p*-nitrodiazobenzene chloride and ethyl-*m*-nitraniline and the second *m*-nitrodiazobenzene chloride and ethyl-*p*-nitraniline. The mode of decomposition of the 187° m. p. ethyl-derivative and the facility with which it breaks up thus negatives the idea which had at first been formed as to this derivative being an amidoazo-compound. A more thorough examination of the substance has shown that it possesses all the characters of a true diazoamido-compound. It gives on complete reduction a mixture of ethyl-*m*-phenylenediamine and *p*-phenylenediamine. A number of the salts of the dinitrodiazoamido-compounds are described in the paper, the chief result to which their examination has led being that only one atom of displaceable hydrogen is present in these compounds. It is pointed out in conclusion that the existence of *three* isomeric ethyl-derivatives containing *p*- and *m*-nitraniline residues is inexplicable by the generally received formula which admits only of the two modifications :—

$(p)NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}Et{\cdot}C_6H_4{\cdot}NO_2(m)$ and $(m)NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}Et{\cdot}C_6H_4{\cdot}NO_2(p)$.

This fact, combined with the difficulty which has hitherto been experienced in accounting for the identity of mixed diazoamido-compounds, has led Professor Meldola to propose a revision of the commonly accepted formulæ of these compounds.

Discussion.

Mr. Groves asked Professor Meldola whether the mixed diazo-compound yielded practically the para- and meta-nitranilines in the same proportions when it was acted on by cold and by hot hydrochloric acid; also whether different preparations of the compound yield the same results—that is, whether the substance is really homogeneous.

Mr. A. G. Green asked Professor Meldola whether the individuality of the compound $C_6H_4(\overset{(3)}{NO_2})\cdot\overset{(1)}{N_2}H\cdot C_6H_4(\overset{(4)}{NO_2})$ and its ethyl-derivative of m. p. 147° was determined with certainty. Considering the tendency which certain nitro-compounds (*e.g.*, *m*- and *p*-nitraniline) have of forming tolerably stable molecular compounds with each other with fixed melting point lower than those of either constituent, it seemed possible that this diazoamido-compound (and its ethyl-derivative) might be such a molecular compound of the two isomers $C_6H_4(\overset{(3)}{NO_2})\cdot\overset{(1)}{N}\cdot NH\cdot C_6H_4(\overset{(4)}{NO_2})$ and $C_6H_4(\overset{(3)}{NO_2})\cdot NH\cdot\overset{(1)}{N_2}\cdot C_6H_4(\overset{(4)}{NO_2})$. This would explain the decomposition by acids into *m*- and *p*-diazonitrobenzene and *m*- and *p*- diazonitrobenzene and *m*- and *p*-nitraniline (or their ethyl-derivatives). The ethyl-derivative of m. p. 147° would then be a compound of the ethyl-derivatives of m. p. 175° and 187°. He suggested that the transference of the N_2-group from one amine to the other (especially in strongly acid solution as given in Professor Meldola's previous paper) might be explained by assuming that an inverse change to diazotisation can occur in a solution of a diazo-compound, resulting in the partial reproduction of the amine and nitrons acid, which latter would then diazotise the second amine.

Professor Meldola, in reply to Mr. Groves, stated that there was no doubt that the so-called unsymmetrical compound was a definite chemical substance and not a molecular combination of the dipara- and dimeta-compounds. This point had been fully considered in the paper, and the experiments which had led to this conclusion were described therein. With reference to the question whether the same quantities of decomposition products were obtained from all the dinitrodiazoamido-compounds when decomposed by acid under similar conditions, he stated that quantitative experiments had not yet been made, but that it was proposed to extend the work in this direction. As far as could be estimated, however, by the appearance of the precipitates (nitrobenzeneazonaphthols) and the nitranilines, it seemed that the compounds all gave about the same results. The question raised by Mr. Green as to the possibility of the unsymmetrical compound being a molecular combination of the other two dinitrocompounds, was substantially the same as that put by Mr. Groves, and did not therefore call for any further reply. With reference to Mr. Green's other suggestion, that diazobenzene salts might by a reverse action be transformed into aniline and nitrous acid, Professor Meldola said that so far as he was aware there was at present no evidence in favour of such a view, and that even if this assumption were granted it would not help to explain any of the difficulties connected with the diazoamido-compounds.

34. "Conjugated Sulphates and Isomorphous Mixtures of the Copper-magnesium-group." By P. C. Roy, B.Sc.

Miss Aston and S. U. Pickering having recently called in question the accuracy of Vohl's conclusions, which are supported by Rammelsberg's investigation of 1854, the author has analysed the following salts, prepared according to Vohl's directions :—

(1.) Nickel-Cobalt-Potassium Sulphate.
(2.) Zinc-Manganese-Ammonium Sulphate.
(3.) Copper-Iron-Ammonium Sulphate.
(4.) Copper-Cobalt-Potassium Sulphate.
(5.) Copper-Magnesium-Potassium Sulphate.

From the result it would appear (1) that whenever two sulphates of the copper-magnesium group are dissolved together in equal molecular proportions, with the requisite quantity of an alkaline sulphate, and the solution is left to evaporate spontaneously salts of the type $x(M''SO_4 + M'_2SO_4 + 6H_2O) + y(M''SO_4 + M'_2SO_4 + 6H_2O)$ are always formed, x and y being small integers. Thus in (1) $x : y = 2 : 1$, in (2) the ratio is as 9 : 2, and so on.

The first crop of crystals as a rule does not conform to Vohl's formula, in fact, in no single instance is there the ratio of equality between x and y. This is strictly in accordance with the behaviour of isomorphous mixtures, for the first crop is always rich in the least soluble component.

The author's conclusions tally with those of Rammelsberg; it is true that his analyses show that in many instances the component sulphates do not occur in *exact* molecular proportions, but this Rammelsberg justly attributes to the fact that it is often difficult to discriminate between any two successive crops.

Discussion.

Mr. Pickering said that Mr. Roy's experimental results entirely confirmed those obtained by Miss Aston and himself, although the conclusions which he deduced from them were very different. It seemed inconceivable that when solutions of the sulphates were mixed in the molecular proportions of 1 : 1 the crystals obtained should consist of the salts in different but still definite proportions, whereas if they were not mixed in this simple proportion the crystals were indefinite in composition. Mr. Roy's own experiments disproved such a view, for after the first few crystals had been deposited the solution would no longer contain the sulphates in the original proportion or 1 : 1, and yet Mr. Roy contended that this solution continued to yield crystals of definite composition. The whole question

depended on whether an analysis of salts containing only 1·3 to 12 per cent. of the metals was sufficiently accurate to determine whether the salt was definite or not. Mr. Pickering considered that it was not so. By taking x and y in the above formulæ to be small integers (not greater than 10) as Mr. Roy does, a formula could be obtained which would represent any indefinite mixture of the sulphates within the limits of analytical error. In the same way the crystals which Mr. Roy obtained from solutions of the copper and nickel salts mixed in indefinite proportions, and to which he says it would be absurd to assign any formula, would correspond exactly with the formula $11CuSO_4,2NiSO_4,13K_2SO_4,78H_2O$, if there were an error of only 0·25 per cent. in the determination of the copper or 0·44 in that of the nickel; errors much smaller than some of those observed in duplicate analysis. The analysis of these salts, therefore, is quite incompetent to determine whether they are definite or not, it is only by performing whole series of experiments that conclusions of any value can be drawn, and these series, as Miss Aston and Mr. Pickering have shown, prove clearly that the composition of the crystals varies continuously with variations in the circumstances under which they are produced.

35. "Suboxide of Silver, Ag_4O." By G. H. Bailey and G. J. Fowler.

The authors have repeated the experiments of Wöhler, and find no evidence of the formation of an argentous citrate when argentic citrate is heated to 100° in a current of hydrogen. The change is a progressive one, the citrate undergoing reduction with the formation of CO_2 and H_2O. In an experiment in which argentic citrate had been exposed to hydrogen at 100° for 36 hours the residue after extraction with ether contained 85·8 per cent. of silver, and by carrying the reduction still further there would in all probability be a complete transformation into metallic silver, water, and carbon dioxide, along with itaconic or the kindred acids. The oxide precipitated from the aqueous extract by means of potash contains metallic silver, and is only obtained in quantities too minute to admit of a determination of the relation of silver to oxygen of sufficiently decisive character.

Faraday's suboxide of silver is also described, and found to be a modified form of ordinary oxide of silver.

Discussion.

Dr. Armstrong pointed out that at the recent Naturforscher-versammlung at Berlin, von der Pfordten of Munich had adduced evidence in favour of the conclusion that an argentous oxide may be obtained.

36. "Action of Trimethylenebromide on the Sodium Compounds of Ethylic Acetoacetate, Benzoylacetate, Paranitrobenzoylacetate, and Acetonedicarboxylate." By W. H. Perkin (junr.), Ph.D.

The sodium compound of ethylic acetoacetate, when treated with trimethylenebromide, is converted into ethylic methyldehydrohexone-carboxylate, $\begin{matrix} CH_3—C——O\diagdown \\ \| \qquad\quad \diagdown \\ COOC_2H_5C\cdot CH_2\cdot CH_2\cdot CH_2 \end{matrix}$, a colourless oil boiling at 225°.

This ethereal salt on hydrolysis yields the corresponding acid, $C_7H_{10}O_3$ (m. p. 118°).

When treated with hydrobromic acid in the cold, the ethylic salt is converted into alcohol, carbonic anhydride, and the bromide of acetobutyl alcohol, thus :—

$$C_9H_{14}O_3 + H_2O + HBr = CO_2 + C_2H_5OH + CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot Br.$$

The free acid, $C_7H_{10}O_3$, on boiling with water, is converted quantitatively into carbonic anhydride and acetobutyl alcohol, thus :—

$$C_7H_{10}O_3 + H_2O = CO_2 + CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH.$$

Similar results were also obtained with the sodium compound of ethylic benzoylacetate; the principal product of the reaction being an ethereal salt of the formula $\begin{matrix} C_6H_5—C——O\diagdown \\ \| \qquad\quad \diagdown \\ COOC_2H_5\cdot C\cdot CH_2\cdot CH_2\cdot CH_2 \end{matrix}$ (crystalline solid, m. p. 60°).

The corresponding acid, $\begin{matrix} C_6H_5—C——O\diagdown \\ \| \qquad\quad \diagdown \\ COOH\cdot C\cdot CH_2\cdot CH_2\cdot CH_2 \end{matrix}$ (m. p. 150°), when treated with hydrobromic acid, yields the bromide of benzoylbutyl alcohol, $C_6H_5\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot Br$, and when boiled with water is decomposed into carbonic anhydride and benzoylbutyl alcohol, $C_6H_5\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$.

Similar derivatives were obtained from ethylic paranitrobenzoylacetate.

The disodium compound of ethylic acetonedicarboxylate, when treated with trimethylenebromide, is resolved into ethylic methyldehydrohexonedicarboxylate, $\begin{matrix} COOC_2H_5\cdot CH_2—C——O\diagdown \\ \| \qquad\quad \diagdown \\ COOC_2H_5\cdot C\cdot CH\cdot CH_2\cdot CH_2 \end{matrix}$ (colourless oil, b. p. 238—240°, 150 mm.).

On hydrolysis this substance is first converted into its acid ethylic salt, $C_{10}H_{14}O_5$ (crystalline, m. p. =114°), and then into the dicarboxylic acid, $C_8H_{10}O_5$ (m. p. 160°).

The acid ethylic salt on distillation splits up quantitatively into

ethylic methyldehydrohexonecarboxylate and carbonic anhydride. The acid, $C_8H_{10}O_5$, when boiled with water, is decomposed into 2 mols. of carbonic anhydride and acetobutyl alcohol, thus :—

$$C_8H_{10}O_5 + H_2O = 2CO_2 + CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH.$$

ADDITIONS TO THE LIBRARY.

Donations.

Proceedings of the Literary and Philosophical Society of Liverpool: vol. xxxix, 1884–85: vol. xl: First Report on the Fauna of Liverpool Bay, 1885–86: from the Society.

Journal of Analytical Chemistry: edited by W. Hart: vol. i, Plate 1: Eaton, Pa., U.S.A.:

Les Soies des Vers Sauvages de l'Inde et leur Emploi dans l'Industrie, par T. Wardle: Paris, 1887:

Essai sur les Propriétés Physiques de la Soie: par N. Roudlot: Paris, 1887: from T. Wardle.

Bulletin of the United States Geological Survey: Nos. 30, 31, 32, 33.

Record of Work done in the Chemical Department of the Owens College, 1857—1887: by Sir H. E. Roscoe: London, 1887: from the Author.

Thomas Young: A Discourse by Professor Tyndall, delivered at the Royal Institution, January 22, 1887: from the Institution.

Yorkshire Philosophical Society: Annual Report, 1887: York, 1887: from the Society.

Bulletin de la Société des Médecins et Naturalistes de Jassy. 1ère Année: No. 1 and 2: from the Society.

At the next Meeting, on April 21st, there will be a ballot for the election of Fellows, and the following papers will be read :—

"The Atomic Weight of Gold." By Professor T. E. Thorpe, F.R.S., and A. P. Laurie, B.Sc., F.R.S.

"The Atomic Weight of Silicon." By Professor Thorpe and J. W. Young, B.A.

"Note on Substitution in the Benzene Series." By Dr. H. F. Morley.

"A Contribution to the Study of Well Waters." By R. Warington, F.R.S.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 37. Session 1887–88.

April 21st, 1887. Mr. William Crookes, F.R.S., President, in the Chair.

Mr. T. H. Redwood was admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Ernest Francis Ehrhardt, B.Sc., Hillcrest, Richmond Hill Road, Edgbaston; Henry Hewetson McMinnes, Agricultural College, Roseworthy, Adelaide, South Australia; John William Young, B.A., Guilford Lodge, Brentwood.

The following were elected Fellows of the Society:—Messrs. W. C. T. Beasley; Edward R. Blundstone, B.A.; Samuel F. Burford; James W. Chenhall; George Collar, B.A.; Henry Danber, jun.; Hugh Gordon; William Gregory; David Lloyd Howard; Edward Rawlins; Louis H. Schubert; Leonard O. Simmons; Samuel Sutcliffe.

The following Papers were read:—

37. "The Atomic Weight of Gold." By T. E. Thorpe, F.R.S., and A. P. Laurie, B.A.

Former determinations of the atomic weight of gold have been made by Dalton, Proust, and Oberkampf, in 1806; Berzelius, in 1813; Pelletier, Javal, and again by Berzelius, in 1844; by Levol, in 1850; and Thomsen, in 1876. The numbers obtained differ widely from each other, partly owing to the unstable character of the salts of gold, and partly to imperfect methods of analysis. The number usually accepted is 196·2, being the value obtained by Berzelius in his second series of determinations, from the analysis of the double chloride of gold and potassium. A special reason for undertaking a revision of

the atomic weight of gold arises from the circumstance that a higher value than that usually assigned to this element is demanded by the periodic law.

The salt employed by the authors is the bromide of gold and potassium, which crystallises readily from water, and (as proved by a series of analyses of different crystallisations) is stable at ordinary temperatures. The salt was prepared by digesting together gold, water, bromine and potassium bromide, and was then three times crystallised.

The method of analysis was as follows:—

About 15 grams of the double salt was introduced into a large porcelain crucible, carefully dried in an air-bath, and then decomposed by heating over a Bunsen flame. The crucible containing the mass of decomposed salt was weighed against a similar and similarly treated crucible, the bromide of potassium washed out with hot water, the solution being drawn into a bottle by reverse filtration, and the gold ignited in a muffle, and again weighed. From these weighings the first set of values for the atomic weight was calculated. A weighed quantity of silver (the purity of which had been tested at the Mint by comparison with the trial plate) was dissolved in dilute nitric acid and added to the potassium bromide, and the excess of the potassium bromide precipitated by a solution of silver nitrate of known strength. From these results the second series of values was calculated. The silver bromide was then collected, dried at 160° C., and weighed. From these weighings a third series of values was calculated.

On comparing the weight of silver used with the weight of bromide of silver obtained, the ratio between them was found to be Ag : AgBr = 1 : 1·74072. According to Marignac, Ag : AgBr = 1 : 74077. According to Stas, Ag : AgBr = 1 : 1·74081. The close agreement of these ratios with that obtained by the authors is a proof of the absence of chlorine in the bromine or potassium bromide employed by them in the formation of the double salt.

The ratios assumed between Ag, Br, K, O, and H were those of Stas, and are as follows:—

Ag	6·7449
Br	4·99634
K	2·44523
O	1
H	0·06265

On the basis of these numbers, the results of the various observations may be thus summarised:—

Series I. (8 *Experiments*).

Au : KBr	37·49137 : 22·61944
„	1·65748 : 1
Au : O	12·3343
Au : H	196·876

Series II. (9 *Experiments*).

Au : Ag.....	41·67403 : 22·79374
„	1·82831 : 1
Au : O.....	12·3318
Au : H	196·837

Series III. (8 *Experiments*).

Au : AgBr.....	36·50997 : 34·76060
„	1·05033 : 1
Au : O.....	12·3322
Au : H	196·842

On the assumption that these values have equal weight, the final value from the whole 25 experiments becomes—

		Diff. from mean.
Series I.....	196·876	+ 0·026
„ II.....	196·837	− 0·013
„ III.....	196·842	− 0·008
Mean	196·850	

When a considerable portion of the determinative work connected with this investigation had been accomplished, a paper on the same subject appeared in the *Berichte* for February, 1887, by Krüss. Krüss also used potassium bromaurate, but his method of treating the salt differed somewhat from ours. The following table contains a summary of his results :—

	Au (H = 1).
I. Au : KBr,Br_3 (9 experiments).....	196·741
II. Au : Br_4 (5 experiments).....	196·743
III. Au : Br_3 (4 „).....	196·619
IV. Au : KBr (4 experiments)	196·620

He also analysed a neutral solution of auric chloride, obtaining the value Au = 196·594.

He adopts as the most probable value Au = 196·64.

Discussion.

The President, after referring to the great value of such investigations, said that he should have been glad to have heard more from the authors regarding their method of weighing, and of the means they had adopted to control the accuracy of their weights, and to correct for the buoyant effect of the air; the errors incidental to the operations of weighing were often greater than the minute errors involved in the chemical operations. The quantities of material used in the various experiments appeared to him to be very small; nevertheless the agreement between the results of the several experiments was highly remarkable.

Professor Thorpe, in reply, said that they had endeavoured to eliminate the corrections necessary on account of buoyancy, and of changes due to deposition of films of moisture, &c., by always using as a tare to the apparatus weighed a precisely similar apparatus which had been treated in the same way. The argument that the same result would have been obtained by means of a single experiment by taking the aggregate amount of salt used in all the experiments together presupposed that the errors of a series of experiments were all in one direction; but this was not the case.

38. "The Atomic Weight of Silicon." By T. E. Thorpe, F.R.S., and J. W. Young, B.A.

The authors have attempted to redetermine the atomic weight of silicon by estimating the quantity of silica yielded by decomposing known weights of silicon tetrabromide by means of water. The results of their experiments are seen in the following table:—

Wt. of $SiBr_4$ *in vacuo*.	Wt. of SiO_2 *in vacuo*.	Si (H = 1).
9·63007 grams.	1·67070 grams.	28·347
12·36099 ,,	2·14318 ,,	28·303
12·98336 ,,	2·25244 ,,	28·347
9·02269 ,,	1·56542 ,,	28·352
15·38426 ,,	2·66518 ,,	28·243
9·74550 ,,	1·69020 ,,	28·325
6·19159 ,,	1·07536 ,,	28·429
9·51204 ,,	1·65065 ,,	28·366
10·69317 ,,	1·85555 ,,	28·364

The aggregate weight of the silicon tetrabromide employed in the various experiments was 95·52367 grams; it yielded 16·56868 grams silicon dioxide. Assuming with Lothar Meyer and Seubert that the

most probable ratios for the atomic weights involved in the calculations are—

Br	4·99721
O.....	1
H.....	0·06265

the above numbers give as the atomic weight of silicon 28·332 if H = 1.

The previously recorded values are all based upon the ratios of equivalent quantities of silicon tetrachloride, silver and silver chloride, and were obtained by using comparatively small quantities, *i.e.*, 1 to 2 grams of the chloride. They are as follows:—

Date.	Authority.	Method.	No. of expts.	Si (H = 1).
1845	Pelouze	$SiCl_4$: Ag	2	28·41
1859	Dumas	$SiCl_4$: Ag	2	27·99
1861	Schiel	$SiCl_4$: AgCl	2	27·99

39. "Note on Substitution in the Benzene Nucleus." By H. Foster Morley.

In an addendum to his paper on "An Explanation of the Laws which govern Substitution in the case of Benzenoid Compounds," Dr. Armstrong says that the formation of metanitro-derivatives on nitration of the sulphates of dimethylaniline, ethylaniline and ethylparatoluidine, while aniline and para-acetyltoluidine produced para- or ortho-derivatives, was due to an increase in the basic powers of nitrogen consequent on the introduction of hydrocarbon radicles in place of hydrogen. The experiments quoted admit, however, of a different explanation, those substances which are mentioned as giving meta-derivatives having been nitrated in presence of a large excess of ice-cold sulphuric acid, the others having been nitrated by a different method.

Dr. Armstrong's hypothesis that meta-substitution is always preceded by combination of the reagent that produces substitution with the radicle already in the benzene nucleus can hardly be maintained in face of such facts as that strong nitric acid converts dimethylaniline into a paranitro-derivative.

We know nothing concerning the cause of formation of meta-compounds; but only that when the group already present is highly chlorous, the new radicle, on entering, takes up the meta-position.

40. "Reply to the Foregoing Note." By Henry E. Armstrong.

It is pointed out that Dr. Morley somewhat misrepresents the author's views. In order to make this clear, the formation of ortho- and para-derivatives is more fully discussed, and an explanation is given of the reasons which led him to think it probable that the behaviour of a compound like dimethylaniline would not in all cases be strictly in accordance with the para-ortho-law. The author considers that Dr. Morley's statement, that "the group $N(SO_4H)H_3$ in aniline sulphate, &c., is more chlorous than NH_2, and hence gives rise to meta-derivatives," is a mere phrase; it in no way follows that such is the case, inasmuch as compounds containing the basic radicle NH_2, or allied groups, and those containing the chlorous radicles Cl, Br, &c., in most respects behave alike.

Discussion.

Mr. Groves, referring to the author's remarks on the action of sulphuric acid on aniline, said that when preparing sulphanilic acid he had been unable to find any intermediate product.

Professor Meldola said that he had repeated many of Nölting and Collins' experiments, and that his results were entirely confirmatory of theirs. In preparing sulphanilic acid on a large scale no intermediate compound was formed, according to his experience.

Dr. Morley said that it appeared to him that the cases quoted by Dr. Armstrong did not serve to substantiate his view any more than those previously advanced.

Dr. Armstrong, replying to Mr. Groves, said that it was not to be expected that an intermediate product such as he had referred to would be noticed in preparing sulphanilic acid. As regards Dr. Morley's criticisms, it was most important to elicit opinions on the subject under discussion, and such criticisms were most welcome; but it was clear that Dr. Morley had failed to understand his views.

At the next meeting, on May 5th, the following papers will be read:—

"A Contribution to the Study of Well Waters." By R. Warington, F.R.S.

"The Influence of Temperature on the Heat of Dissolution of Salts in Water." By Prof. Tilden, F.R.S.

"Crystals in Basic Slag." By J. E. Stead and C. H. Ridsdale.

"The Distribution of Lead in the Brains of two Factory Operatives dying suddenly." By A. Wynter Blyth.

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No. 38. Session 1887–88.

May 5th, 1887. Mr. William Crookes, F.R.S., President, in the Chair.

Messrs. T. Cooksey, George Robertson, David Wilson, Jun., and George Collar were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Hugh Barclay, Rose Hill, Harrington, Cumberland; John Edward Green, 68, Portland Road, Holland Park, W.; William Marshall, 7, Walter Street, Nottingham; Frederick Lawrence Overend, B.A., Blair Lodge School, Polmont, N.B.; J. Stanley Phillips, Wentworth, Upper Long Ditton, Surrey; Walter Shelley Spencer, 142, Clifton Street, Brooks Bar, Manchester; Charles Ernest Stedman, Williamstown, Melbourne.

The following Papers were read:—

41. "A Contribution to the Study of Well Water." By R. Warington, F.R.S.

The proportion of chlorine in the rain water at Rothamsted is 2 per million; the proportion of total combined nitrogen about 0·7 per million.

Of 31 inches of rain, annually falling on a bare clay soil, 17 inches have evaporated and 14 inches percolated below 5 feet. Drainage chiefly occurs between October and February. The quantity of chlorine in the drainage from 5 feet of soil is the same as that in the rain, but the proportion is doubled in consequence of evaporation. The proportion of nitrogen as nitrates in the drainage water from 5 feet of bare clay soil has averaged 10·7 per million. The produc-

tion of nitrates in the soil is chiefly during summer; the principal discharge of nitrates as drainage is in the autumn.

When land is covered with vegetation evaporation is increased, and the winter drainage commences at a later period. Evaporation being increased, the chlorine in the drainage water may also be increased. The drainage from the Rothamsted unmanured wheat land contains 6 per million of chlorine; the drainage from the plot manured with farmyard manure, 7·3 per million. While vegetation is active no nitrates are found in the drainage water from the unmanured wheat; the nitrates reappear in autumn, after harvest. The average proportion of nitrogen as nitrates in the drainage from unmanured wheat is 3·4 per million; from wheat receiving farmyard manure, 5·8 per million. These are minimum numbers. With rain containing the amount of chlorine found at Rothamsted, the average proportion of chlorine in drainage water can hardly exceed 8 per million.

The pure well waters of Harpenden contain a minimum of 4·4 of nitric nitrogen per million; this, therefore, is the average amount in the drainage water of the district.

The deep wells in the chalk of Harpenden derive their main supply from a flow of underground water proceeding from north-west to south-east. Each well has besides its own local drainage. The pure well waters contain about 11 per million of chlorine; this amount does not sensibly vary throughout the year. Wells contaminated by sewage are generally at their maximum purity in October. They may show a commencement of a rise in chlorides one or two months after active autumn drainage has commenced. All through the drainage season, the effect of one month's drainage is not manifested in the well water till the following month. The maximum of chlorides in the contaminated wells occurs after the end of the drainage season—usually in March. The nitrates and chlorides increase at a nearly equal rate during the early months of the drainage season. If active drainage continues for three months, a great increase in the proportion of nitrates will usually then take place, and this relative excess of nitrates is maintained for some months. The proportion of nitrates to chlorides varies considerably in different contaminated wells. The sewage for poorly fed population yields a high proportion of chlorides to nitrates. Stable sewage furnishes apparently a high proportion of nitrates to chlorides. The old sewage contamination of deep wells is generally more or less chloric, chlorides being more permanent than nitrates.

The well waters of Harpenden contain the nitrifying organism in small proportion; it is probably derived from surface soil which has fallen in.

In the contaminated waters the quantity of silica is not increased,

and the quantity of carbonates but little increased. Lime is considerably increased, and magnesia still more. Nitrates, chlorides and sulphates are largely increased.

On comparing the low proportion of chlorine found in the pure chalk waters of Harpenden, near the edge of the London basin, with the amount found in other chalk waters, and especially with the chalk waters beneath the London clay; and considering further the proportion of chlorides which can possibly be contributed by rain: it appears highly probable that a portion of the chlorides in chalk water, and probably in the water of other strata, is derived from a residue of sea-salt remaining in the rock.

The proportion of nitrates found in the waters of uncontaminated wells and springs in the permeable strata of England is fairly constant; it indicates an average loss to the soil of about 7 lbs. of nitrogen per acre per annum.

42. "Crystals in Basic-Converter Slag." By J. E. Stead and C. H. Ridsdale.

The authors describe a variety of crystals found near the centre of blocks of basic-converter slag, weighing 40—50 cwts. each, which had cooled slowly.

No. 1. Large, well-formed, flat square crystals of a faint-yellowish colour, consisting essentially of the phosphate $4CaO{\cdot}P_2O_5$; these have also been described by Hilgenstock.

No. 2. Blue crystals, previously noticed by Groddeck and Brockmann; these appear to be a double calcium silicate and phosphate, $CaO{\cdot}P_2O_5{,}CaO{\cdot}SiO_2$. Vanadium protoxide was present to the extent of 1·64 per cent.

No. 3. Feathery or fern-like crystals; these are remarkable as they contain under 4 per cent. of acid oxides and over 95 per cent. of basic oxides—chiefly of calcium, magnesium, iron (protoxide and peroxide) and manganese.

No. 4. Hexagonal, needle-shaped lemon-coloured crystals, which appear to consist of about 86 per cent. $4CaO{\cdot}P_2O_5$ with 10—11 per cent. of silicates of metallic oxides.

Nos. 5 and 6. Two varieties of flat black needles, the one magnetic, the other not. No. 5 contained about 10 per cent. $CaO{\cdot}Al_2O_3$, 45 per cent. $3CaO{\cdot}Fe_3O_4$ and 33·5 per cent. $3CaO{\cdot}Fe_2O_3$. No. 6 contained about 15 per cent. $CaO{\cdot}Al_2O_3$ and 73 per cent. $3CaO{\cdot}Fe_2O_3$.

Discussion.

In reply to a question by Mr. Thompson, Mr. Ridsdale stated that Mr. Meiers had determined the crystalline forms of the substances

which had been described, and had examined them in polarised light. In reply to Mr. Nettlefold, he said that they were of opinion that the whole of the phosphorus was present as $4CaO{\cdot}P_2O_5$.

43. "Note on the Influence of Temperature on the Heat of Dissolution of Salts in Water." By William A. Tilden, D.Sc., F.R.S.

In a paper which appears under this title in the April number of the Transactions, Mr. Pickering reviews the experiments which he had previously published upon the same subject, and so far modifies the conclusions which he had drawn from those experiments as to admit that the lines representing the heat of dissolution of various salts at successive temperatures do not consist of a series of curves following one another at irregular intervals. But Mr. Pickering maintains that the new experiments now published lead to a result which only differs in degree from his former conclusion and involves admissions which are essentially of the same character as those which he has abandoned. His main conclusion will be best expressed in his own words (p. 335) :—"The heat of dissolution of a salt increases uniformly with the temperature up to a certain point, when the rate of increase is suddenly lowered, and this fresh rate continues uniform till lowered again at some higher temperature," &c.

The consequence of this is that the graphic representation of the results must, according to the author, consist of two or more straight lines, which in the cases which he has examined, and within the limits of temperature to which his experiments have been confined, meet at 8—10°, or in some cases at higher temperatures. And although the suggestion was made by Dr. Alder Wright, at the discussion which followed the reading of the paper, that the results might be represented by continuous curves without these breaks, the author deliberately rejects this suggestion, and adds a postscript to his paper emphasising his own view.

The experimental work upon which this conclusion is based is, if not quite unimpeachable, at any rate of a high order of excellence, surpassing any other published work on the same subject within my knowledge. It is only in the interpretation of the results that I venture to differ from Mr. Pickering, but I think it is so plain that his main proposition is untenable, that I feel it desirable to direct attention to the question whilst the work is fresh in the recollection of the Society.

Without any desire to be hypercritical, I think some exception might be taken to the way in which the means appear to have been arrived at. Instead of taking the arithmetical means of the values resulting from experiments performed at the several temperatures,

the mean results have been deduced from the lines representing the various series, whether experiments were done at all the points or not (p. 304). The effect of this is naturally to straighten out the line between temperatures where experiments were not made.

I may also remark that in the statement of the differences (post-script, p. 336) between the values calculated from the equation for the curve and the author's values, the word "observed" values must be understood as these "mean" observed values which are not the exact mean values for each temperature. But after all this way of calculating affects the values of the mean to a very small extent, and has not destroyed their significance. Taking Mr. Pickering's own figures as representing the mean experimental results at the successive temperatures, and simply plotting them out on squared paper, I submit that inspection is sufficient to show that every one of his series conforms to a continuous curve, which, considering the difficulties of the work, is generally quite remarkably smooth and free from irregularities.

With reference to potassium chloride, the author remarks (p. 304) that "the sixteen mean results from 10—25° inclusive evidently form a straight line," and that the experiments below 9° form another straight line. To this I demur. I do not see how such an idea could have arisen, unless it was from the differences tabulated on p. 306, from which it appears that the increase in the value of M per degree drops from 50 cal. between 8° and 9° to 42 cal. between 9° and 10°. Looking at other parts of the table, however, it will be noticed that even greater irregularities occur, as for instance—

at 16—17°	the difference is	33	cal.
17—18	,,	45	,,
18—19	,,	36	,,

If a fall of 8 cal. at 8° to 9° is held to justify the assumption of a break in the line at this point, why should not another break be accepted when there is a rise of 12 cal., or a fall of 9 cal. in the rate at the temperatures referred to?

Similar remarks apply in other cases. Potassium nitrate, for example, shows a change in the rate of increase—

from	40	cal. at	12—12°
to	23	,,	13—14

It is not clear why the break should be introduced here, when at only one degree higher there is a change of greater amount, viz.:—

from	23	cal. at	13—14°
to	42	,,	14—15

and yet no corresponding change is recognised in the curve.

In discussing these curves, I have added the graphic representation of all the experiments, in order that they may be compared with the means, and that no injustice may be done to the author's view.

Again in the case of sodium chloride the mean differences given in the table (p. 308) seem to indicate, if any, four rather than two straight lines, the value being—

3—7°	44·5 cal.
7—11°	38·0 ,,
11—18	31·7 ,,
18—25	29·5 ,,

Though the curves are somewhat irregular in some of the other cases, especially that of sodium carbonate, the hypothesis of sudden breaks is not supported sufficiently to make it acceptable in the face of all the probabilities pointing the other way. Such irregularities might naturally be expected in work of this nature, surrounded with difficulties as it is.

Mr. Pickering criticises severely the results I obtained in the attempt to get determinations of the heat of dissolution over a considerable range of temperature. I am indebted to Mr. Pickering for reminding me of the necessary validity of the formula of Person, which shows the dependence of thermochemical effects upon temperature. The discrepancy between the calculated values in that paper and the experimental results arose from the mistake of assuming the values for the specific heats of the several solutions to be practically constant throughout, whereas they increase with rise of temperature, though to an extent which, according to the experiments of Marignac, is very small, from about 20° C. to 50°. But this does not destroy the experimental numbers which, though subject to a general error which makes them all somewhat too low, are consistent among themselves, and support the conclusion that the rate at which the heat of dissolution is influenced by temperature diminishes as the temperature rises. Fortunately this accords with the results of Mr. Pickering's own work, whether we do or do not adopt the hypothesis which he prefers, that the changes occur suddenly. In my opinion all the probabilities, in addition to Mr. Pickering's own results, indicate that the heat of dissolution of a salt in water is a continuous function of the temperature.

Discussion.

Mr. Pickering, in reply, said that, after a very careful re-examination of his results, he found it impossible to accept Professor Tilden's interpretation of them. In the first place he defended the method which he had employed in deducing mean values: this consisted in

separately plotting each series of experiments by drawing lines to connect the various values of each series, and deducing the final mean by taking the mean of the values given by these lines at each degree; and it was to be noted that the means were not deduced from the lines representing the individual series after the irregularities in them had been smoothed out, as in the dotted lines in Plate I, as Professor Tilden appeared to think they were—probably through a want of clearness in the explanation given at p. 304 of the speaker's paper. The method described would give unfair results in the event of one series containing a far larger number of determinations than another, and to avoid this he had never applied the method when a greater interval than 2° separated the successive experiments in any series. Though not perfect, this method is certainly the fairest which can be adopted, and beyond comparison much fairer than that suggested by Professor Tilden. Two series, consisting of experiments at alternate degrees and free from any experimental error, except that made in standardising the thermometers (which would cause the results of one series to be uniformly above, and those of the other uniformly below the truth), would each yield a straight line, if such were the nature of the true results, whereas their mean deduced by Professor Tilden's method would be a wavy line, and was obviously incorrect.

Mr. Pickering said, that the concordance between his results and the curve or straight line method of representing them was so close that it was quite impossible by mere inspection of a diagram to decide which method was the best. The whole question depended on the magnitude of the average error in the two cases, and Professor Tilden had brought forward no numbers to show that a curve indicated a smaller error than straight lines. On the other hand, Mr. Pickering had examined the average error in the two cases very carefully. In the additional note to his paper he had shown that a curve (deduced from the actual results just as the straight lines were deduced from the actual results) did not agree with the mean results so well as his straight lines; in the six cases which he examined the curve would represent a very considerable increase in the average error, and at the same time the sign of the error in the individual experiments was not positive and negative promiscuously as in the straight line diagram, but errors of like sign were grouped together, the numbers deduced from the curve being above the actual results throughout a considerable range and then below them throughout another considerable range.

Mr. Pickering had examined in the same way the results of each individual series performed with potassium chloride; the average errors, according to the two methods of representing the results, were :—

	Straight line.	Curve.
'08A	4·7 cal.	5·3 cal.
'61A	4·0 „	5·7 „
'08B	1·3 „	4·7 „
'61B	4·6 „	—

Thus in every case the curve did not represent the results so closely as the straight line. With series '61B the "curve" equation obtained represented a practically straight line.

Another way in which he had attempted to investigate the question was to find the equations which represented those portions of the diagram which he considered straight (from 9—25° with potassium chloride), and to see whether they gave a curve which could by any means represent the other results (below 9°). The various values of β in the equation to the curve $(1 + \alpha t + \beta t^2)$ which he obtained were—

Mean of 9 equations from series			'08A	+ 0·094
„	8	„	„ '61A	− 0·056
„	2	„	„ '08A	+ 0·094
„	2	„	„ '61A	+ 0·674
Mean (weighted according to number of experiments included)				+ 0·025

which value represents a line so nearly straight that it would deviate from straightness by only 4 cal. from 9—25°, or 6 cal. from 3—25°, whereas the actual results show a deviation of 152 cal. between these last-mentioned limits. The results from 9—25° are, therefore, not conformable with those from 9—3°. Thus in every way in which the results are examined they undoubtedly favour the straight line as opposed to the curve method of representation.

In answer to Professor Tilden's question referring to the results given in Table I, Mr. Pickering said that he thought it obvious why he should have taken the increase of 42 to 50 cal. (9—8°) as significant of a true alteration in the rate, and should not have regarded the diminution of 45—33 cal. (18—17°) as having any significance at all: in the latter case the difference of 45 cal. is evidently an exceptionally high result, unsupported by any other observation, which when combined with the differences immediately preceding and following it (36 and 33 cal.) gives the same mean as 16 differences from 25° to 9°, whereas the difference of 50 cal., while higher than any differences preceding it, is identical with the mean of the five differences which succeed it (8—3°).

He thought that no theoretical speculation should induce us to reject the more correct method of representing his results in

favour of the less correct method. Finally he pointed out that, although the influence of temperature on any chemical change is represented by a curve, this curve really occupies but a very small proportion of a diagram representing the effect of temperature from the absolute zero to the highest known temperatures, and that this diagram consists of practically straight lines inclined to each other at different angles, and joined by curves, presenting an appearance, when reduced to the same scale, precisely analogous to that which he considered his dissolution results presented.

44. "The Distribution of Lead in the Brains of two Factory Operatives Dying Suddenly." By A. Wynter Blyth.

At a certain lead factory in the East of London five cases of more or less sudden death at different dates have been attributed to the effects of lead. In two of the cases the author had an opportunity of making a toxicological investigation. In the one case 24·25 mgrms. of lead sulphate was separated from the liver and 5·4 mgrms. from one kidney; there was also lead in the brain.

In the second case investigated, occurring about a year after the first, the brain was more exhaustively examined, the cerebrum and cerebellum being treated separately and divided up by suitable means into white matter, kephalin, ether extract, substances soluble in cold alcohol and albuminoid residue, and the lead determined in each.

	Cerebrum, 460·8 grams.	Cerebellum, 156·2 grams.
Aqueous extract	1·1 mgrms.	0·4 $PbSO_4$.
White matter (kephalin-free)	—	5·0 „
Kephalin	1·5 „	6·0 „
Ether extract (from which kephalin had been precipitated)	—	—
Substances soluble in cold alcohol	—	—
Albuminoid residue	40·0 „	6·0 „

Calculated on the whole cerebrum this would amount to 99·7 mgrms., or a possible total for the whole brain of 117·1 mgrms. $PbSO_4$.

There has hitherto been no reasonable hypothesis to explain the profound nervous effects of the assimilation of minute quantities of lead, but if it is allowed that lead forms definite compounds with essential portions of the nervous system, it may then be assumed that in effect it withdraws such portions from the body; in other words, the symptoms are produced not by poisoning in the ordinary sense of the term, but rather by destruction—a destruction it may be of important nerve centres.

45. "Researches on Silicon Compounds and their Derivatives. A New Chlorobromide of Silicon." By J. Emerson Reynolds, M.D., F.R.S.

In purifying a large quantity of silicon tetrabromide prepared by means of crude bromine, the author has separated a portion boiling at 140—141°, of the relative density 2·432, which analysis shows to be the chlorobromide of the formula $SiBr_3Cl$.

Titles of Papers of interest to Chemists recently read before Societies in the United Kingdom:—

"Processes of Refrigeration." By J. J. Coleman.

"Chemical Affinity and Solution." By Mr. Wm. Durham.

"Researches on Micro-organisms, including Ideas of a new Method for their Destruction in certain cases of Contagious Disease." By Dr. A. B. Griffiths.

"The Increase of Electrolytic Polarisation." By Mr. W. Peddie.

"Further Determinations of the Effect of Pressure on the Maximum Density Point of Water." By Professor Tait.

"Note on Hoar Frost." By Mr. John Aitken.

"On the Influence of Certain Rays of the Solar Spectrum on Root Absorption and the Growth of Plants." By Dr. A. B. Griffiths.

"On Ice and Brine, and on the Distribution of Temperature in the Antarctic Ocean." By Mr. J. Y. Buchanan.

"Note on Cobaltic Alums." By Mr. Hugh Marshall.

"On the Physical Properties of Methyl Alcohol." By Professor Dittmar and Mr. C. A. Fawsitt.

"On the Instability of the Double Salts, $M''SO_4,R'_2SO_4,6H_2O$, of the Magnesium Series." By Professor Dittmar.

"A Diatomaceous Deposit from North Tolsta-Lews." By Mr. John Rattray.

Royal Society of Edinburgh, Jan.—May, 1887.

At the next Meeting on May 19th there will be a ballot for the election of Fellows, and the following Papers will be read:—

"The Formation of Hyponitrates." By Professor Dunstan and T. S. Dymond.

"Ozone from pure Oxygen; its Production and its Action on Mercury, with a Note on the Silent Discharge of Electricity." By W. A. Shenstone and J. T. Cundall.

"The Thermal Results of Neutralisation and their Bearing on the Nature of Solution and the Theory of Residual Valency." By S. U. Pickering.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 39. Session 1887–88.

May 19th, 1887. Mr. William Crookes, F.R.S., President, in the Chair.

Messrs. S. F. Benford, Edgar Hall, J. S. Jackson and Hugh Gordon were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. William Bott, Ph.D., Owens College, Manchester; William Nathaniel Evans, 66, Stackpole Road, Bristol; Khasberao B. Jadhara, Baroda, Bombay Presidency, India; J. M. Kavanagh, Victoria Mill, Herbert River, North Queensland; John T. Sheard, Gas Offices, Bloom Street, Salford; Henry Livingstone Sulman, 13, Brewster Gardens, St. Quintin Park, W.; Frederick Percy Watson, 31, Carholme Road, Lincoln.

The following Papers were read:—

46. "The Formation of Hyponitrites." By Professor Dunstan and T. S. Dymond.

Zorn (*Ber.*, **15**, 1258) has stated that alkali nitrites and nitrates are readily acted on by ferrous hydroxide, forming hyponitrite, ammonia, nitrogen and nitrous oxide. Divers and Haga (Trans., 1884, 87, and 1885, 364) allege that alkali nitrites yield much ammonia, but neither hyponitrite nor hydroxylamine, nor any gaseous product; and that alkali nitrates are wholly unaffected; while nitric oxide in presence of alkali is to a large extent converted into ammonia by ferrous hydroxide, but yields no hyponitrite.

The authors find that nitric oxide in the absence of alkali is reduced by ferrous hydroxide to nitrous oxide and nitrogen; no ammonia or hyponitrite is formed. In the presence of an alkali (sodium hydroxide),

nitric oxide is partly reduced to nitrous oxide and nitrogen, and partly absorbed; the solution contains hyponitrite and ammonia, but on standing with excess of ferrous hydroxide it evolves nitrogen, and the hyponitrite disappears. The amount of hyponitrite formed depends within certain limits on the quantity of alkali which is present, on the quantity of ferrous hydroxide used, and on the time during which action is allowed to proceed. When three formula weights of ferrous hydroxide, $Fe(OH)_2$, and one of nitric oxide are used, the quantity of hyponitrite formed increases with each formula weight of sodium hydroxide that is added. About 20 per cent. of the nitric oxide may be converted into sodium hyponitrite.

Alkali nitrites and ferrous hydroxide readily interact, producing nitrogen, nitrous oxide, ammonia and hyponitrite. The amounts which are formed of these substances depend on the quantity of ferrous hydroxide used, and also on the time during which the action continues. Excess of ferrous hydroxide after some time converts sodium nitrite entirely into nitrogen and ammonia. As a lecture experiment, it is recommended to dissolve 5 grams of ferrous sulphate in about 25 c.c. of water, and to precipitate the liquid with sufficient of a 10 per cent. potash or soda solution to leave the mixture faintly alkaline; 1 gram of sodium nitrite dissolved in about 25 c.c. of water is then added, and the mixture stirred. After effervescence has ceased, and the liquid has stood for about half an hour, it is filtered. If the filtrate is diluted with an equal volume of water, and carefully neutralised with acetic acid, on the addition of silver nitrate a pale yellow precipitate of silver hyponitrite (mixed with some silver nitrite) will be obtained. Or a few drops of a silver nitrate solution may be added to the liquid before neutralisation; but in this case the precipitate will rapidly darken in colour. Alkali nitrates are hardly at all affected by ferrous hydroxide; small quantities are slowly converted into ammonia.

In explaining their results, the authors draw attention to the simultaneous formation of hyponitrite and hydroxylamine when sodium amalgam acts on dissolved sodium nitrite. They show that the ammonia is not derived from a further action of sodium amalgam on the hyponitrite, which yields only nitrogen. Similarly, ferrous hydroxide liberates nitrogen from sodium hyponitrite, but no ammonia is formed.

They consider that the action of sodium amalgam on a solution of sodium nitrite is best explained by supposing that the sodium nitrite combines with two hydrogen-atoms, forming $NaN(OH)_2$.

This compound may decompose, yielding hyponitrite: $NaN(OH)_2 = NaNO + H_2O$; or it may undergo reduction, yielding hydroxylamine, $NaN(OH)_2 + 2H = NaOH + NH_2OH$, and also ammonia and

nitrogen, $4NaN(OH)_2 + 10H = 4NaOH + N_2 + 2NH_3 + 4H_2O$. Ferrous hydroxide, it is suggested, acts in the same way, being a substance which will combine with the hydroxyl of water when sodium nitrite is present to unite with the hydrogen. Any hydroxylamine which may be formed will at once be converted into ammonia by ferrous hydroxide. The authors find that when excess of ferrous hydroxide is used, and nitrogen and ammonia are the only products, the reaction takes place almost exactly in accordance with the equations (i) $4NaNO_2 + 8OH_2 + 8Fe(OH)_2 = 4NaN(OH)_2 + 8Fe(OH)_3$; (ii) $8NaN(OH)_2 + 6OH_2 + 14Fe(OH)_2 = 8NaOH + 3N_2 + 2NH_3 + 14Fe(OH)_3$. Since nitric oxide in presence of alkali yields exactly the same products as nitrites, the change can be most readily explained in the same way, assuming that the compound $NaN(OH)_2$ is first formed.

47. "Ozone from Pure Oxygen." By W. A. Shenstone and J. Tudor Cundall.

The authors describe an apparatus in which oxygen has been prepared and stored without the possibility of air gaining admittance. So far as it is possible to determine the purity of the gas by tests, it would appear certain that it has contained at most $\frac{1}{5000}$ of nitrogen. The oxygen has been collected and sealed up in glass tubes containing phosphoric oxide, in contact with which it has been kept for periods ranging from eight weeks to eight months. Subsequently it has been submitted to the action of electricity, and the ozone produced has been measured. In one experiment made at 10° C. no less than 11·7 per cent. of the oxygen taken was converted into ozone. This is a very considerably higher proportion than has been obtained either by Brodie or by the authors from ordinary oxygen when similar means of electrification are employed, but not so high as was obtained by Andrews and Tait, who, however, worked in a different way, and the exact value of whose results is uncertain in consequence of the tendency of the sulphuric acid that they used in their gauges to absorb ozone.

The action of dry ozone on dry mercury has also been studied. Dry ozone from pure oxygen is decomposed in the well-known manner by pure and dry mercury, but without visible oxidation of the mercury. Further, when a definite volume of oxygen is ozonised and afterwards left in contact with mercury for many hours, the oxygen almost entirely recovers its original volume, the small differences observed between the initial and final volumes being probably due to the difficulty of measuring oxygen with accuracy in a tube partly coated with mercury.

The authors point out that the apparently high yield of ozone obtained under somewhat unfavourable conditions as to temperature may be due—

1. To the absence of nitrogen, the presence of which Andrews has shown is, under some conditions, very unfavourable to the production of ozone.

2. To the character of the electric discharge, which is most free from large sparks when the air and glass surfaces from which the discharge takes place are free from moisture.

The paper concludes with a note on the character of the silent discharge of electricity in ozone generators of the Siemens type, the influence of dryness on the character of the discharge being discussed.

Very full details are given of the method they now employ for preparing and storing pure oxygen. The method might readily be adopted in the case of other gases that do not attack mercury. The apparatus was chiefly constructed for the production of pure gases for various other experiments on the action of electricity on gases that are still incomplete.

48. "The Volumetric Relations of Ozone and Oxygen." A Lecture Experiment. By W. A. Shenstone and J. Tudor Cundall.

Soret and Brodie have shown that if v be the contraction produced on the electrification of a mass of oxygen, then $2v$ will represent the further contraction that will occur on absorbing the ozone formed by means of turpentine. If it be true that ozone completely dissolves in turpentine, this indicates that three measures of oxygen are concerned in the formation of two measures of ozone. The authors describe an apparatus which they have constructed for readily exhibiting Soret's observation to a class.

Discussion.

The President said that he had been accustomed to join tubes *in situ* in the manner described by Mr. Shenstone. He added that it was possible to join together two different kinds of glass by means of a little soft white enamel, such as could be obtained from Powell's.

Mr. Fairley had also joined tubes in the manner described by the authors; calling attention to Brodie's ozonising apparatus, he remarked that the tube used by Brodie was probably thinner than was used by the authors.

Dr. Armstrong thought that the results of the authors' experiments on the action of mercury on ozone were a valuable contribution to our knowledge of the influence of minute amounts of third bodies on the course of chemical change. He suggested that it was important, if possible, to determine the extent to which oxidation took place in

presence of varying minute amounts of moisture, in order to ascertain if this exercised an influence comparable with that exhibited in Prof. H. B. Dixon's experiments on the rate of propagation of the explosive wave in a mixture of carbonic oxide and oxygen.

Mr. Shenstone said that experiments such as were suggested by Dr. Armstrong, although very difficult with mercury, might probably be carried out with silver, which effected the decomposition of ozone with extraordinary facility. In reply to the question put by Mr. Page, he was quite unable to account for the peculiar condition assumed by the mercury when submitted to the action of the ozone. He had not been successful in joining tubes with the aid of the enamel spoken of by the President, but on the other hand had found it easy to join even combustion tubing to soft glass by means of an oxyhydrogen jet.

49. "On the Thermal Phenomena of Neutralisation and their bearing on the Nature of Solution and the Theory of Residual Affinity." By S. U. Pickering.

In dilute solutions the heat of neutralisation of an alkali is a constant quantity, independent of the nature of the alkali; and the majority of acids give the same results with any given base, whence it follows that $M,R,Aq - M,'R,Aq = M,R',Aq - M',R',Aq$, where M and R are electropositive and electronegative radicles respectively. Each term of this equation is made up of two quantities, M,R (heat of formation of the salt molecule) and MR,Aq (true heat of dissolution of the salt), and it is impossible that such a relationship should exist were these actions independent of each other; they must be part of one quantity, and as M,R is a chemical action, so also is MR,Aq. The affinity of M and R are not entirely saturated by their combination with each other, and it is only by the further combination of the compound with water that saturation becomes complete. The equation can obtain only if the water satisfies the residual affinity of either the non-metallic or the metallic atom, and in the event of atomic valencies being whole numbers, all the terms of the equation will be equal, whereas if these valencies are not whole numbers the equation will be made up of two pairs of equal terms.

The recognition of the heat evolved in any action being an absolute measure of the affinities saturated is necessitated by a study of these thermal results.

The few cases in which acids have a higher heat of neutralisation than the majority may be explained by their residual affinity being in excess of that which water can saturate; while in those cases where abnormally low results are obtained the salt is probably partially dissociated by the water.

Owing to the heat of neutralisation being independent of the nature

of the base, it follows that the heat of formation in solution of similar salts of two different metals differs by a constant quantity, whatever the non-metallic radicle may be.

Discussion.

With reference to the hypothesis submitted to the Society in 1885 by Mr. Pickering, that the valency of an atom is never a whole number, but slightly smaller or larger, Dr. Armstrong remarked that it was impossible at present to put any such hypothesis to the test, owing to the complexity of the phenomena which had to be interpreted. On the other hand, the hypothesis to which attention had been directed by Helmholtz, in the last Faraday lecture, involved a precise and clear conception—that of a definite unit-valency, and was a necessary deduction from Faraday's law of electrolysis: in the speaker's opinion there was as yet no other course open than to consider the facts in the light of this hypothesis. He was, however, entirely of Mr. Pickering's opinion with regard to the interpretation to be given of the thermal values obtained on neutralising dilute solutions, having already, in fact, as Mr. Pickering had pointed out in his paper, used the same argument in reply to Dr. Nicol in the course of the discussion on the nature of solution at the meeting of the British Association at Birmingham. Dr. Nicol did not appear to have recognised its force, to judge from the remarks at the conclusion of his paper in the current part of the Transactions; and disregarding the evidence afforded by the heat-evolution on dissolution of many salts—which can only be due to one cause, viz., to association of the dissolved substance with water—claims, in support of his contention that hydrates do not exist in solution, the results of the thermal study of changes which it is almost beyond doubt are of a complex character, and which have hitherto remained uninterpreted.

50. "The Action of Metallic Alkylates on Mixtures of Ethereal Salts and Alcohols." By T. Purdie, Ph.D., B.Sc., Professor of Chemistry in the University of St. Andrews.

The author having observed (Trans., 1885, 855) that the ethylic salts of fumaric, cinnamic and oxalic acids are converted into the corresponding methylic salts by the action of a solution of sodic methylate in methylic alcohol, finds that the reaction in question is of general application: that is to say, when a mixture of an alcohol with an ethereal salt containing a different alcoholic radicle from that of the alcohol is treated with small quantities of sodic or potassic alkylate, an interchange of radicle takes place between the alcohol and the ethereal salt; and that the chemical change exhibits in a marked degree the character of continuous action. It is supposed

that the reaction is effected by the continuous formation and decomposition of a compound of the ethereal salt with the alkylate.

Besides the cases mentioned above, a similar reaction is found to occur when minute quantities of alkylate are added to the following mixtures: methylic oxalate with ethylic alcohol; amylic oxalate with ethylic or methylic alcohol; and ethylic oxalate with amylic alcohol.

Also in the case of mixtures of amylic acetate with ethylic or methylic alcohol; ethylic acetate with amylic alcohol; and phenylic acetate with ethylic alcohol.

A series of blank experiments to which no alkylate was added was performed for purpose of comparison. While the extent of interchange of alcoholic radicle occurring in the latter is usually small, the interchange in the former amounts under similar conditions frequently to 50 per cent., and in some instances is almost quantitatively complete.

Discussion.

Dr. Armstrong remarked that, as Prof. Purdie had not failed to point out, the exchange of radicle occurring between the ethereal salt and the alcohol is most probably effected by the alternate production and decomposition of an additive compound formed by the union of the salt with the alkylate, in the manner suggested by him in a "Note on the Action of Sodic Ethylate on Ethylic Oxalate and other Ethereal Salts," communicated to the Society in January, 1874 (*Ber.*, **7**, 129). Several applications of the principle involved in this explanation were to be found in the edition of vol. iii of *Miller's Chemistry* by Mr. Groves and himself (at pp. 861, 907, 923), and the formation of ethylic acetoacetate from ethylic acetate and sodium ethylate was there represented (p. 909) by equations identical with those recently put forward as original by Claisen and Lowman; whose experiments throw as much, but no more, light on the genesis of the acetoacetate as Geuther's original experiments—a fresh proof that these last are still not rated at their proper value. It was remarkable also that it was not generally recognised that sodium ethylate, not sodium, was the effective agent in transforming ethylic salts, W. Wislicenus having, for example, in his recent paper represented the change effected by sodium in mixtures of ethylic salts as directly due to the sodium, and as involving the formation of sodium substitution-derivatives. The additive compound of the sodium alkylate with the ethereal salt had been represented by himself and others as an atomic compound, the assumption being made that the elements of the alkylate became distributed; it might be pointed out that it was, perhaps, unnecessary to make this assumption, it being conceivable that change would supervene if once the alkylate became associated with the ethereal salt without its elements becoming distributed.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

United States Geological Survey: Monographs, XI: Geological History of Lake Lahontan: by J. C. Russell: Washington, 1885. from the Director of the Survey.

Journal of the College of Science: Imperial University of Japan: vol. i, Part I (*cont.*): Tokio, 1886: from the University.

Colonial and Indian Exhibition: Reports on the Colonial Sections: Edited by H. T. Wood: London, 1887: From the Commission of the Exhibition.

United States Geological Survey: Mineral Resources of the United States, 1885: Washington, 1886: from the Director of the Survey.

The Work of the Imperial Institute: by Sir F. A. Abel: London, 1887: from the Author.

Nitrate of Soda; its Importance and Use as a Manure: by A. Stutzer: London, 1887: from the Publisher.

Cellulose: by C. F. Cross and E. J. Bevan: edited by W. R. Hodgkinson: London, 1885: from the Authors.

New Commercial Plants and Drugs. No. 10: by T. Christy: London, 1887: from the Author.

II. *By Purchase.*

Official Year Book of the Scientific and Learned Societies of Great Britain and Ireland: London, 1887.

Principien der Organischen Synthese: von E. Lellmann: Berlin, 1887.

Fortschritte im Probirwesen: von C. A. Balling: Berlin, 1887.

Vorträge über die Entwicklungsgeschichte der Chemie: von A. Ladenburg: 2 ed.: Braunschweig, 1887.

RESEARCH FUND.

A meeting of the Research Fund Committee will be held in June. Fellows desiring grants are requested to make application before June 11th.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 40. Session 1887–88.

June 2nd, 1887. Mr. William Crookes, F.R.S., President, in the Chair.

The President announced that the Council had resolved to present an Address of Congratulation to the Queen.

Certificates were read for the first time in favour of Messrs. William Elborne, Owens College, Manchester; and Herbert B. Stocks, 13, Peet Street, Liverpool.

The following Papers were read:—

51. "The Equivalent of Zinc." By Lieut.-Colonel Reynolds, late R.E., and Professor W. Ramsay.

The determination has been made by measuring the hydrogen evolved on dissolving zinc in acid, every precaution being taken to ensure accuracy; the weight of the hydrogen obtained was deduced from Regnault's determination of the density of hydrogen. The zinc used was separated by electrolysis from zinc sulphate purified to the utmost possible extent; the last sample prepared was so nearly pure that dilute acid would scarcely act on it.

In all 29 experiments were made. Four experiments had to be rejected; nine were not fully corrected, and therefore were also rejected; the next 11 were considered preliminary, the mean atomic weight deduced from them being 65·2430; finally, five experiments were completed, and the following results obtained from these are free from all known sources of error:—

	65·5060
	65·4766
	65·4450
	65·5522
	65·4141
Mean.....	65·4787 ± 0·016135

Full details are given in the paper.

52. "The Magnetic Rotation produced by Chloral, Chloral Hydrate and Hydrated Aldehyde." By W. H. Perkin, Ph.D., F.R.S.

The author has shown in a previous paper (*Chem. Soc. Trans.*, 1886, 777) that when water unites with another substance so as to produce an atomic and not a molecular compound the magnetic rotatory power of the product is less than the sum of the magnetic rotatory powers of the compounds used in its formation. He has now applied the same method of examination to aldehyde and chloral and their hydrates.

Chloral hydrate was examined (*a*) in the fused state at 55·5°; and at the ordinary temperature (*b*) dissolved in water in the proportion of 1 mol. to 3 mols. of water, and (*c*) dissolved in a new neutral liquid-isoamyl oxide. Deducting from the values found that deduced for liquid chloral, the results are as follows:—

	Fused at 55·5°.	In water.	In amyl oxide
Chloral hydrate....	7·173	7·016	7·028
Chloral	6·590	6·590	6·590
	0·583	0·426	0·438

From these numbers it is evident that chloral hydrate does not contain water as a constituent, as in that case the difference should be 1·00.

As ethylidene glycol, $CH_3{\cdot}CH(OH)_2$, is not known at any rate in a pure state, its magnetic rotatory power was deduced from that of some of its derivatives (*Chem. Soc. Trans.*, 1884, 571). Deducting from the most probable value (2·817) that of aldehyde (2·385), a difference results (0·432) which is practically identical with those found in the case of chloral hydrate at low temperatures. The result obtained with fused chloral hydrate at 55·5° is a little higher, but there is no doubt that the hydrate is slightly dissociated when heated to this temperature: that this is the case is further indicated by a series of determinations of the density of a solution of chloral hydrate in amyl oxide between 4° and 60°, a change in the curve obtained on

plotting the results being seen to occur at a point corresponding to a temperature a good deal below 55·5°.

Experiments were also made with mixtures of aldehyde and water, that generally used consisting of equimolecular proportions. On making this mixture of aldehyde and water, some interesting peculiarities were noticed. If the temperature of the air and of the liquids be about 8° or 9°, at the moment of mixing the temperature drops about 1·5°; it then commences to rise somewhat quickly, and continues to rise, but more and more slowly, for a long time; in one experiment, made in a large test-tube covered with cotton-wool, commencing at 9° the temperature rose to 18·7° but only in the course of 25 minutes. If the temperature of the substances before admixture be about 16° and the quantities not too small, the rise of temperature is more rapid and the mixture enters into ebullition.

On attempting to determine the density of the mixture of aldehyde and water, the results obtained were at first very perplexing from the fact that concordant numbers could not be obtained. It was then found that when any change of temperature took place the volume did not become constant in less than two and a half to three hours, so that in determining the density it was necessary to keep the tube containing the mixture at the desired temperature for two and a half hours before adjusting. Part of the product evidently undergoes dissociation as the temperature rises, recombination taking place as the temperature falls, but only very gradually, a small variation of temperature sufficing to produce a disturbance.

Comparing the magnetic rotatory power of aldehyde with that of the mixture with water at 16°, the difference $0{\cdot}929 = 3{\cdot}324 - 2{\cdot}385$ is less than 1·00, and it may therefore be concluded that combination takes place; at a lower temperature no doubt this combination would have been found to be more perfect. There can, however, be no doubt that ethylidene glycol is present in the mixture.

Glycols are viscid fluids, and it is interesting to notice that when the hydrated aldehyde is shaken up, a froth forms which does not break at once, the mixture differing in this respect from aldehyde and also from water.

The effect of mixing aldehyde and absolute alcohol in molecular proportions is also very interesting. If the temperature of the liquids be not too low, the temperature rapidly rises and the mixture boils; if however the temperatnre be low, say 8° or 10°, the temperature immediately falls seven or more degrees: the rise then sets in, and before long the mixture reaches its boiling point. In the first instance the fall is due to what may be called molecular arrangement setting in between the two fluids, which is a physical change, and occurs before chemical action has had time to take place to any

appreciable extent; then chemical action takes place more and more rapidly, and in consequence the temperature rises.

On mixing pure dry ether with aldehyde a fall of temperature occurs; subsequently the temperature rises gradually, but only to that of the surrounding air.

53. "Note on a New Class of Voltaic Combinations in which Oxidisable Metals are replaced by Alterable Solutions." By C. R. Alder Wright and C. Thompson.

It appeared to the authors probable that just as a liquid capable of parting with oxygen, chlorine, &c., can be used in conjunction with an electrode of unchangeable material at one side of a voltaic cell (as in Grove's nitric acid battery and analogous combinations), or may be replaced by a solid conducting electrode, itself capable of losing oxygen (*e.g.*, a plate of strongly compressed peroxide of lead), so conversely might a conducting plate of oxidisable material (*e.g.*, zinc) at the other side be replaced by an unchangeable electrode in conjunction with a liquid capable of taking up oxygen, chlorine, &c., without producing any fundamental change in the character of the actions taking place in the cell whilst generating a current. The electrode immersed in this oxidisable substance, like the zinc of an ordinary cell, would acquire the lower potential, and the opposed plate the higher potential; *i.e.*, the wire connected with the latter would be the "positive pole" of the construction in reference to the external circuit.

On trial, it has been found that such is the case, and that in consequence a large variety of novel forms of cell becomes easy of construction. For example, sodium sulphite or potassium ferrocyanide solution opposed to chromic-sulphuric acid solution; preferably with an intermediate layer of some neutral salt solution, such as sodium sulphate, to prevent the direct action of the two fluids on one another. During the passage of a current, sodium sulphate or potassium ferricyanide is formed in quantity proportionate to the electricity passing, *i.e.*, to the amount of silver thrown down in a silver voltameter included in the circuit; whilst chromium sulphate is produced at the other side. Various analogous cells are described, in particular one where lead oxide dissolved in caustic soda is opposed to alkaline hypobromite: in this case lead dioxide is produced and separates out in the solid form; and one where chromium sesquioxide dissolved in caustic soda is opposed to chromium trioxide dissolved in sulpuric acid; here sodium chromate and chromium sulphate are formed, an E.M.F. about equal to that of a Daniell cell being set up.

Discussion.

Mr. Page said that after listening to Dr. Wright he was able for the first time to understand how electric currents might arise in the animal body.

Dr. Alder Wright said in reply to Mr. Page that the experiment suggested of opposing venous and arterial blood had not been actually tried by him as yet, but he thought it quite probable that a weak current might be produced (the President subsequently said that he had been told—he believed by Mr. Peter Squire—that a current was produced on opposing venous and arterial blood). By opposing alkaline pyrogallol solution to oxidising agents, notable currents could be developed; and various other organic compounds might be used instead of pyrogallol. With certain organic bodies, however (*e.g.*, chloral hydrate), attempts to produce oxidation in cells had hitherto failed. The opposition of acid and alkaline fluids alone would not necessarily produce more than infinitesimal currents; Becquerel's "*pile à oxygène*" (nitric acid opposed to caustic potash solution) gave rise to decomposition of nitric acid and evolution of oxygen from the electrode immersed in the alkali; other authors had found that analogous cells with chromic-sulphuric acid instead of nitric acid would behave in the same way and develop a continuous current capable of doing external electrolytic work, such as deposition of silver in a voltameter; on the other hand, a cell in which caustic soda and sulphuric acid only were opposed (so that chemical action other than neutralisation could not take place) would only develop an infinitesimal current through a silver voltameter, capable of depositing only traces of silver even after some days, although its E.M.F. measured by an electrometer was considerable.

With regard to the observations of Dr. Armstrong, he would say that whilst without doubt Grove's gas battery was the prototype of the class of cells discussed, inasmuch as that combination was virtually an oxidisable solution of hydrogen opposed to an oxidising solution of free oxygen, still the examination of cells in which other oxidisable fluids were used instead of hydrogen solution, and other oxidising substances besides solution of oxygen, was a branch of experiment in which hardly anything had hitherto been done, and which seemed to merit some little attention. The authors desired to study in detail the general behaviour of certain typical classes of cells in which actions of the kind take place, especially from the point of view of elucidating the precise chemical changes going on and their relations to the amounts of electrical (or current) energy developed. Whilst there was not exactly a probability of any very startling discovery being made, there were still a number of points of interest connected

with the subject worth examining; and although the hope of an improved primary battery based on actions of this kind for commercial use, as suggested by the President, was perhaps not yet within measurable distance, yet the problem of economically obtaining current energy by direct chemical action (and especially by oxidation) was one now attracting considerable attention, and it was impossible to predict what might or might not be the result of systematic experiments tending in that direction. The importance of obtaining practically usable currents from coal direct without the use of the steam engine and dynamo could hardly be over-rated should it hereafter be found practicable so to do; and in view of the compactness of the animal machinery, whereby the oxidation of fuel in the form of food gave rise by muscular action to mechanical energy, it did not seem to be of necessity hopeless to attempt to solve such a problem.

54. "The Composition of Prussian Blue and Turnbull's Blue." By Edgar F. Reynolds.

According to Williamson, these compounds are respectively represented by the formulæ Fe_7Cy_{18} and Fe_5Cy_{12}, but Reindel and others have conjectured that they are identical in composition. The author has carefully prepared Prussian blue from hydrogen ferrocyanide and ferric chloride, and Turnbull's blue from hydrogen ferricyanide and ferrous sulphate; his analyses of the products show that Williamson's formulæ are correct expressions of their composition.

55. "Phlorizin." By Professor E. H. Rennie, D.Sc.

The author has endeavoured by a re-examination of phlorizin to decide as to the correctness or otherwise of the usual formula, and also to ascertain whether the sugar yielded by it on hydrolysis is really dextrose or not. He shows by analyses and by a quantitative examination of the decomposition by dilute sulphuric acid that the usually accepted formula and equation correctly describe the composition and hydrolysis of phlorizin. The sugar obtained from it melted at 85—86°; its molecular rotatory power was $[\alpha]_D = 57{\cdot}9°$; and it gave with phenylhydrazine hydrochloride a yellow crystalline precipitate melting at 204—205°: there can be little doubt, therefore, that it is ordinary dextrose.

56. "Further Notes on the Chemical Action of *Bacterium aceti*." By Adrian J. Brown.

The author has continued his studies on the oxidising actions of *B. aceti*, and states that although mannitol has been shown to be

easily converted into lævulose by the organism, its isomeride, dulcitol, is not acted upon.

The dihydric alcohol, glycol, is oxidised into glycollic acid, no other product being formed. The action is carried on much further when calcic carbonate is present to neutralise the acid as it is formed.

The trihydric alcohol, glycerol, is found to be completely decomposed into carbon dioxide and water, the only other product formed being a very small amount of an acid the identity of which could not be determined. Glycerol appears to encourage the growth of *B. aceti* more than any other substance with which the author has experimented.

The tetrahydric alcohol, erythrol, resists the action of the organism. Attention is called to the fact that erythrol and methylic alcohol are both acted on by oxygen in presence of platinum-black, but escape oxidation when placed under the influence of *B. aceti;* it is also shown that when the same substance is submitted to oxidation in the two ways, the products are generally dissimilar, as in the cases of mannitol and dextrose. It is therefore considered that although the products of the actions which occur in presence of both platinum-black and *B. aceti* are similar, in the case of ethylic alcohol the manner in which the oxidation is effected, contrary to the usual idea, is probably quite different.

Mannitol has been prepared by the author from pure dextrose by the action of sodium amalgam. On submitting this to the action of *B. aceti* it was converted into lævulose, thus completing the conversion of dextrose into lævulose. As the melting point and crystalline form of mannitol from dextrose are similar to those of mannitol from manna, there can be little doubt that the two mannitols are identical.

57. "Note on the Cellulose formed by *Bacterium xylinum*." By Adrian J. Brown.

The author showed in a previous paper (*Chem. Soc. Trans.*, 1886, 432), that the acetic ferment *B. xylinum* is able to convert lævulose into cellulose. On treating this cellulose with strong sulphuric acid, it is found to be converted into a dextrorotary sugar, and in this respect to resemble ordinary cellulose.

58. "The Oxidation of Ethyl Alcohol in the Presence of Turpentine." By C. E. Steedman, Williamstown, Victoria.

The author finds that dilute ethyl alcohol in the presence of air and turpentine becomes oxidised to acetic acid. The experiment was made by placing in a clear glass 16-oz. bottle a mixture of 2 drams of alcohol, 1 dram of turpentine, and 1 oz. of water; the bottle was

securely corked and left exposed to a varying temperature averaging about 80° F. for three months; at the end of that time the liquid was strongly acid from the presence of acetic acid.

One curious fact appears to have light thrown upon it by this observation. Mr. McAlpine, Professor of Biology at Ormond College, Melbourne University, has a method of preserving biological specimens by abstracting their moisture with alcohol after hardening in chromic acid, and then placing the specimen in turpentine for some time; great discrepancies arise, however, according as the alcohol is allowed or not to evaporate from the specimen before dipping it into turpentine.

At the next Meeting on June 16th *there will be a ballot for the election of Fellows*, and the following Papers will be read:—

"The Thermal Constants of a Liquid Mixture." By Professor Ramsay and Dr. S. Young.

"Derivatives of Hydrindonaphthene and Tetrahydronaphthalene." By W. H. Perkin, jun.

"The Formation of Closed Carbon-chains." By F. S. Kipping, B.Sc., Ph.D., and W. H. Perkin, jun.

"The Action of Ethylene Bromide on Ethylic Acetoacetate." By P. C. Freer, Ph.D., and W. H. Perkin, jun.

"Derivatives of Pentamethylene." By H. E. Colman, B.Sc., and W. H. Perkin, jun.

"Derivatives of Hexamethylene." By P. C. Freer, Ph.D., and W. H. Perkin, jun.

"An Attempt to Synthesise a Ring containing Seven Carbon-atoms." By the same.

"Researches on the Laws of Substitution in the Naphthalene Series." By Dr. Armstrong.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 41. Session 1887–88.

June 16th, 1887. Mr. William Crookes, F.R.S., President, in the Chair.

Mr. William Henry Coates was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. George Carrington, B.A., Missenden Abbey, Great Missenden, Bucks; Yoshimosa Koga, Imperial Mint, Osaka, Japan; William Henry Richardson, Dudley; Arthur Walley Warrington, Dinglefield, Dingle Lane, Liverpool.

The following were elected Fellows of the Society:—

Messrs. Hugh Barclay, William Bott, L. C. Daniell, Ernest Francis Ehrhardt, William Nathaniel Evans, Frederick William Freeman, Edward Day Gravill, Herbert James Gover, John Edward Green, Richard Nelson Jones, M.R.C.S., Khasberas B. Jodhara, J. M. Kavanagh, William Marshall, Henry Hewetson McMinnes, Fred. Lawrence Overend, B.A., J. Stanley Phillips, John T. Sheard, Walter Shelley Spencer, Charles Ernest Stedman, Henry Livingstone Sulman, Frank Traphagen, Ph.D., Frederick Percy Watson, and John William Young, B.A.

The President announced that the following Address had been presented to Her Majesty:—

TO THE QUEEN'S MOST EXCELLENT MAJESTY.

May it please Your Majesty,

On the happy completion of the fiftieth year of your Most Gracious Majesty's reign we, the President, Council, and Fellows

of the Chemical Society, established in 1841 and incorporated under a Charter granted in the 12th year of your Majesty's reign, desire to present to your Majesty our sincere congratulations and to express our loyal devotion to your August Person and to your Throne.

We humbly submit, amidst the general rejoicing, that we have special reason to rejoice in the growth of Science, and particularly of Chemical Science, which characterises your Majesty's wise and beneficent reign. If it be borne in mind to what an extent the applications of Chemistry are now essential to the prosperity and the security of your Majesty's Empire, this development assumes a truly national importance.

Chemistry is of no nationality, yet the names of Black, Cavendish, Dalton, Davy, Faraday, and Graham fully testify to the vigour of its growth on British soil. From a variety of causes, however, its cultivation in this country during the second quarter of the century seemed to be falling into neglect, and it is to His Royal Highness the late Prince Consort that the nation is very largely indebted for its revival.

The turning point in the history of Chemical Science in your Majesty's Dominions was the foundation of the Royal College of Chemistry in the year 1845. To the success of this College the Prince Consort contributed, not merely by his personal munificence and by consenting to become its first President, but more particularly by using his influence to overcome the obstacles in the way of the appointment of its first Professor.

The result cannot be exaggerated; indeed, a majority of British Chemists of the younger generation are directly or indirectly the pupils of that College, while the discoveries in Chemical Science of its Students may well rank amongst the most brilliant achievements of your Majesty's reign.

If Chemical Science in this country is no longer ignored, but is recognised as essential to national prosperity, if Chemistry has won its rightful place in the curriculum of the higher education, and if laboratories properly organised for the conduct of this intellectual discipline are to be found in British Universities, Colleges, and Schools, these happy changes are mainly due to the exertions and influence of the late Prince Consort and to the impulse given by the Royal College of Chemistry in response to his encouragment. The Prince Consort's enlightened zeal in the furtherance and development of Science in the country of his adoption is universally recognised, and we rejoice to find, that His Royal Highness the Prince of Wales treads in the footsteps of his illustrious Father.

It is our most earnest prayer that your Most Gracious Majesty may long be spared to reign over a happy, loyal, prosperous, and

united empire, and that your Majesty's enlightened and beneficent example may steadily be followed and held in grateful remembrance.

We remain, with profound respect,

YOUR MAJESTY'S MOST FAITHFUL SERVANTS.

The following Papers were read:—

59. "A Study of the Thermal Properties of a Mixture of Ethyl Alcohol and Ethyl Oxide." By William Ramsay, Ph.D., and Sydney Young, D.Sc.

The authors have previously shown that for both the gaseous and the liquid states, the relation of pressures to temperatures at constant volume may in the case of methyl and ethyl alcohols, ethyl oxide and carbon dioxide, and presumably in the case of all stable liquids, be expressed by the formula $p = bt - a$; *i.e.*, the isochoric lines, or lines of equal volume, for unit mass of the substance, are straight when mapped against pressures as ordinates and temperatures as abscissæ. They also showed that in the case of the two dissociating substances, acetic acid and nitric peroxide, such isochoric lines are not straight, but are, at large volumes, tangential to the theoretical isochoric lines of minimum density at higher temperatures, and at lower temperatures probably tangential to the theoretical isochoric lines of maximum density. A comparison of the behaviour of such stable and dissociable substances has shown the effect of chemical union on the relations of pressure, temperature and volume. But the mixture of two liquids, such as alcohol and water, is known frequently to be accompanied by contraction and by evolution of heat. It therefore appeared of interest to thoroughly investigate the behaviour of such a mixture in order to throw light on the nature of this attraction.

Experiments were therefore made with a view to determining the relations of volume, pressure and temperature between wide limits with a mixture of alcohol and ether, of which, individually, the constants have already been obtained.

The most striking conclusions are (1) the dependence of pressure during condensation on volume, so that the vapour-pressures are represented not by a line but by a band; (2) the curvature of the isochoric lines at temperatures and pressures near the condensing points of the mixture; (3) the great alteration of volume under certain conditions on mixing the two bodies, amounting, on the one hand, in some circumstances to a contraction of 4 per cent., and in others to an expansion of 115 per cent.

Discussion.

Professor Dewar said that in dealing with the historical part of the subject the authors of the paper had in his opinion omitted to do full justice to the work of Amagat and other investigators. A short time ago, Messrs. Ramsay and Young had communicated a paper to the Royal Society, entitled "A Preliminary Note on the Continuity of the Liquid and Gaseous States of Matter," which had been referred to that evening, purporting to contain a discovery which was nothing more than a simple elementary deduction from Van der Waals' formulæ representing the continuity of the gaseous and liquid states of matter. The Van der Waals formula had been improved upon by Clausius; in its original form, however, it was still sufficient to account for Andrew's isothermal law and Amagat's law of the limiting volume of a gas under high pressure: two of the most important experimental deductions from a vast number of observations. Professor Amagat in continuing his work had discarded all antecedent theoretical views, and had confined his attention to the approximate laws he could deduce from the experimental facts. He had long ago given the equation that Messrs. Ramsay and Young evidently thought important enough to embody in the form of a paper. In dealing with this subject the mass of calculations made by the authors may satisfy some views, but real progress in this department of physico-chemical inquiry can only be made by reaching greater accuracy in the measurements; always assuming that the substances examined are pure. Endless repetitions of details can only cumber the ground, not clear it.

The experiments on the critical volume of PH_4Cl, to which Dr. Young referred, were in reality made by a pupil of the speaker (Mr. Skinner), and had already been published.

Dr. Young, in reply, said that the work of Amagat and others was referred to in the paper, but owing to the short time at his disposal he had been unable to do full justice to the history of the subject that evening. Although Van der Waals' formula could be converted into theirs, the converse was not the case; moreover, Van der Waals' formula did not represent the facts.

60. "Derivatives of Hydrindonaphthene and Tetrahydronaphthalene." By W. H. Perkin, Jun., Ph.D.

The author describes experiments which have enabled him to prepare from *ortho*xylene derivatives of the closed chain hydrocarbons

$$C_6H_4{<}\begin{matrix}CH_2\\CH_2\end{matrix}{>}CH_2 \quad \text{and} \quad C_6H_4{<}\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}{>}$$

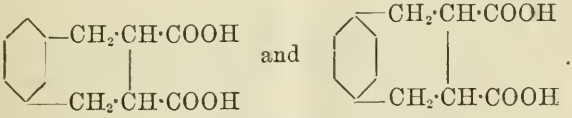
Hydrindonaphthene. Tetrahydronaphthalene.

Hydrindonaphthenedicarboxylic acid was obtained from the ethylic salt formed by the action of the dibromide, $C_6H_4(CH_2Br)_2$—prepared by heating orthoxylene with bromine at 125°—on the disodium-derivative of ethylic malonate, $CNa_2(COOEt)_2$; when heated at 200°, this acid is resolved into carbon dioxide and hydrindonaphthenecarboxylic acid.

Tetrahydronaphthalene-derivatives were obtained in two ways: 1. By the action of orthoxylylene dibromide on the disodium-derivative of ethylic acetylenetetracarboxylate, $\begin{matrix} CNa(COOEt)_2 \\ CNa(COOEt)_2 \end{matrix}$; and (2) as the end result of the following series of changes—ethylic sodiomonochloromalonate, $CNaCl(COOEt)_2$, having been submitted to the action of orthoxylylene dibromide; the resulting compound, $C_6H_4[CH_2{\cdot}CCl(COOEt)_2]_2$, was digested with zinc-dust and acetic acid, and the chlorine having been displaced by hydrogen, the product was converted into the disodium-derivative, $C_6H_4\left\{\begin{matrix} CH_2{\cdot}CNa{\cdot}(COOEt)_2 \\ CH_2{\cdot}CNa{\cdot}(COOEt)_2 \end{matrix}\right.$, which on treatment with iodine gave the theoretical amount of tetrahydronaphthalenetetracarboxylate. On heating the tetracarboxylic acid at 200°, it is resolved into CO_2, water, and the anhydride of tetrahydronaphthalenedicarboxylic acid; on dry distillation of the silver salt of this latter acid, naphthalene is produced together with the anhydride of tetrahydronaphthalenedicarboxylic acid, silver, CO_2, and water.

61. "The Synthetical Formation of Closed Carbon Chains in the Aromatic Series." By F. S. Kipping, B.Sc., Ph.D.

The author describes experiments which were instituted with the object of ascertaining whether it would be possible, by substituting meta- and para-xylene for ortho-xylene, to obtain isomeric tetrahydronaphthalene-derivatives of the formulæ—



The method of procedure was the same as that described in the previous paper. Meta- and para-xylylene dibromides were each treated with ethylic sodiochloromalonate, the product was reduced with zinc-dust and acetic acid, and the reduction product was converted into the sodium-derivative, which was treated with bromine.

The reaction appeared to take place with perfect regularity, sodium

bromide separating; but on examination it was found that the greater part of the product consisted of the unchanged substance, and no new closed chain compound could be detected. It is difficult to understand what really takes place in these reactions, or what the precise action of the bromine on the sodium compound is.

Discussion.

Dr. Miller thought that since the authors had not yet proved even the possible existence of rings consisting of 7 and 8 carbon atoms, the experiments quoted by them could not be considered as proof that ring-formation from two side-chains attached to a benzene nucleus depends solely on *position*. The chain of 6 carbon atoms in the ortho-compound, $C_6H_4<\begin{matrix}CH_2\cdot CNa(COOEt)_2\\CH_2\cdot CNa(COOEt)_2\end{matrix}$, might be expected to yield a ring composed of 6 carbon atoms, because such rings are not only possible but possess very great stability. There is, however, nothing surprising in the fact that the chains of 7 and 8 carbon atoms in the corresponding meta- and para-compounds do not yield corresponding rings, especially when considered in conjunction with Dr. Perkin's other unsuccessful attempt to produce a ring containing 7 atoms of carbon. The well-known property possessed by so many ortho-derivatives of readily yielding anhydro- and other ring-derivatives is without doubt a function of the 1 : 2 position, but whether this is so in the case of the above-mentioned compound cannot be regarded as proved.

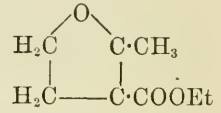
Indeed it is conceivable that the length of the side-chains may be an important factor in determining the condensation. It would be interesting to ascertain whether an *ortho*-derivative of similar constitution to the above, but containing an additional atom of carbon in each side-chain, would also yield a ring-derivative; if not, it would be an argument that ring formation depends on *length* of chain as well as position.

Dr. Kipping said, in reply, that he had anticipated the objection raised to the theoretical conclusions he had deduced from his experiments. He had, therefore, tried a number of experiments on the action of metaxylylene bromide on the sodium-derivative of ethylic malonate. If a reaction analogous to that which resulted in the formation of hydrindonaphthene-derivatives from orthoxylylene bromide were to take place, a compound should have been formed containing a ring consisting of *six* carbon-atoms, in which, however, the junction was effected to carbon-atoms in the meta-position. In no case, however, could such a substance be obtained. It, therefore, appeared to him that the main reason why ring formation did not take place when

meta- and para-derivatives of benzene were used, was that the side-chains were not in a suitable position.

62. "The Product of the Action of Ethylene Bromide on Ethylic Acetosodacetate." By P. C. Freer, Ph.D., and W. H. Perkin, Jun., Ph.D.

The compound formerly described by W. H. Perkin, Jun., as ethylic acetyltetramethylenecarboxylate having been proved to contain a carbon-oxygen-ring, being an anhydride of a carboxylate of acetobutylic alcohol, it was thought advisable to examine the product of the action of ethylene bromide on ethylic acetosodacetate, in order to finally settle the nature of the compound known as ethylic acetyltrimethylene carboxylate. Ethylene bromide interacts with ethylic acetosodacetate, forming a compound, $C_8H_{12}O_3$, to which the following formulæ are applicable :—

$CH_2:CH\cdot CH\begin{cases}Ac\\COOEt\end{cases}$ $\quad$ $\begin{matrix}CH_2\\CH_2\end{matrix}>C\begin{cases}Ac\\COOEt\end{cases}$ $\quad$ 

That the first is inapplicable has been shown in a previous publication; further experiments show that the product is to be regarded as a mixture of the compounds represented by the latter two formulæ. That this is the case is proved by the decomposition of the acid obtained from the ethereal salt; if this be distilled, CO_2 is given off, and an oil passes over, separable into two substances, one boiling at 112°, which is insoluble in water, even after standing for weeks; the other boiling 20° lower, which gradually dissolves in water, forming acetopropylic alcohol. It is therefore safe to regard the ethereal salt $C_8H_{12}O_3$ as a mixture of ethylic acetyltrimethylenecarboxylate with a compound which it is proposed to call ethylic *methyldehydropentonecarboxylate*.

The acids obtained on hydrolysing the ethereal salt just referred to are decomposed on boiling with water into CO_2 and acetopropylic alcohol. This reaction is in entire accordance with the character of the trimethylene-ring, as shown in the change of trimethylenedicarboxylate into carbobutyrolactone.

The ether $C_8H_{12}O_3$ readily combines with hydrogen bromide, forming ethylic ω-bromethylacetoacetate, a change which is likewise in accordance with the behaviour of the other trimethylene compounds.

If this latter compound be boiled for some hours with dilute muriatic acid, it is quantitatively converted into alcohol, CO_2, HBr, and acetopropylic alcohol. Acetopropylic alcohol is easily reduced by sodium amalgam, being converted into γ-pentylene glycol.

63. "Derivatives of Pentamethylene." By H. G. Colman, B.Sc., and W. H. Perkin, Jun., Ph.D.

γ-Pentylene glycol, $CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2(OH)$, is converted by the action of HBr into the corresponding γ-pentylene dibromide, $CH_3{\cdot}CHBr{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br$.

When this bromide is mixed with ethylic sodiomalonate in alcoholic solution the following reaction takes place:—

$$2CHNa(CO_2Et)_2 + CH_3{\cdot}CHBr{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br = CH_2\begin{<}CH_2{\cdot}CH{\cdot}CH_3 \\ CH_2{\cdot}C(CO_2Et)_2\end{>} + CH_2\begin{<}CO_2Et \\ CO_2Et\end{> + 2NaBr.$$

Ethylic methylpentamethylenedicarboxylate is a pleasant-smelling oil, b. p. 243—244°. The corresponding acid is crystalline, and melts at 173—175°, decomposing into CO_2 and methylpentamethylene-monocarboxylic acid. The latter is a colourless liquid which boils at 220°; it possesses a penetrating smell similar to that of butyric acid.

64. "The Synthesis of Hexamethylene-derivatives." By P. C. Freer, Ph.D., and W. H. Perkin, Jun., Ph.D.

Hitherto all attempts to synthesise hexamethylene-derivatives have been unsuccessful owing to the impossibility of obtaining a pentamethylene dibromide of the formula $CH_2Br{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHBr$, which could be submitted to the action of ethylic sodiomalonate. The authors have, however, succeeded in preparing a homologue of the desired bromide from acetobutylic alcohol, $Ac{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2OH$. This alcohol is readily reduced to δ-hexylene glycol by means of sodium amalgam, as Lipp has shown. This glycol is completely converted by treatment with hydrogen bromide into δ-hexylene dibromide, $CH_3{\cdot}CHBr{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br$, which interacts with ethylic sodiomalonate, forming ethylic methylhexamethylenedicarboxylate,

$$CH_3{\cdot}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}C(COOEt)_2.$$

65. "An Attempt to Synthesise Heptamethylene-derivatives." By P. C. Freer, Ph.D., and W. H. Perkin, Jun., Ph.D.

If δ-hexylene dibromide, $CH_3{\cdot}CHBr{\cdot}(CH_2)_3{\cdot}CH_2Br$, be treated with two molecular proportions of ethylic sodiomalonate, the tetracarboxylate, $(COOEt)_2CH{\cdot}CH(CH_3){\cdot}(CH_2)_4{\cdot}CH(COOEt)_2$, is produced. It appeared probable that if the disodium-derivative of this compound

were treated with bromine a closed chain heptamethylene-derivative would result. This, however, was found not to be the case, the action taking place in some other manner not yet made out.

Discussion.

Dr. Armstrong said that the problem which Dr. Perkin and his associates were endeavouring to solve was one of great theoretical importance. In representing the compounds which had been described as derivatives of closed-chain hydrocarbons, they were undoubtedly formulating what would appear to be the simplest interpretation of the synthetical methods adopted; but there was little independent conclusive evidence to support their view. In several respects the behaviour of the compounds was by no means that of closed-chain derivatives; thus it was remarkable that the trimethylene-ring should be easily split by hydrogen bromide and by water, but not by bromine. If, however, a closed carbon chain could be split by such means, the conditions realised in the case of the trimethylene-compound described by Freer and Perkin were certainly those which would tend most to favour such a change. In illustration of the difficulty of determining whether a compound was saturated, the speaker referred to xeronic acid, which Fittig had represented as the derivative of a closed chain of 4 carbon-atoms, but which has recently been proved to be a diethylfumaric acid. Assuming that the compounds described were closed-chain derivatives, the failure to obtain a heptamethylene-derivative gave weight to Dr. Miller's objection to Dr. Kipping's argument, and justified the conclusion that the number of carbon-atoms as well as position had to be taken into account.

Dr. Japp referred to the hydrocarbon prepared by Burton and himself from anhydracetonebenzil (*Chem. Soc. Trans.*, 1887, 423); it is highly probable that this is a tetra- or penta-methylene-derivative, and it is noteworthy that it does not undergo any change if heated with iodhydric acid and phosphorus at 150°.

66. "The Composition of Shale-spirit." By A. K. Miller, Ph.D., and T. Baker, B.Sc.

The authors have sought to determine (*a*) whether shale-spirit contains any higher olefines than those found in the liquid mixture of hydrocarbons from oil-gas, and (*b*) the constitution of the olefines, Armstrong and Miller having shown that heptylene was the highest hydrocarbon of the C_nH_{2n} series present in oil-gas products, and that all the olefines from oil-gas possess a normal constitution.

The shale-spirit was fractionally distilled, and the three fractions

boiling respectively at 140—145°, 120—125°, and 75—85°, were examined by the method described by Armstrong and Miller (*Chem. Soc. Trans.*, 1886, 74). Each fraction was found to consist of paraffin to the extent of about 50 per cent., the remainder being partly olefine and partly less unsaturated hydrocarbons of unknown constitution. The bromine addition-compounds of the latter are to a large extent decomposed by distillation in a current of steam, yielding tarry products, whilst the olefine bromides distil over unchanged. After distilling the bromides under reduced pressure, the olefines were recovered by the zinc-copper couple; they were then fractioned; and finally the fatty acids produced by their oxidation with potassium permanganate were examined.

The results obtained show that not only the lower olefines, but also octylene and nonylene are present in shale-spirit. The nonylene was readily obtained in a state of comparative purity, and its oxidation-products indicated it to be the pure normal olefine, heptylethylene. The lower olefines were, however, more difficult to purify, and gave a more complex mixture of oxidation-products. The octylene fraction (b. p. 120—122°), for instance, gave both heptylic and caproic acids (the latter in larger quantity), together with acetic and formic acids; and in the same way the hexylene fraction (65—70°) was found to yield more butyric than valeric acid, these being also accompanied by formic and acetic acids. In the same way as the production of heptylic and formic acids indicates the presence of normal octylene, the formation of caproic and acetic acids might be regarded as evidence that an isomeric octylene is also present; but this is not necessarily the case, as acetic acid appears to be a constant product of the oxidation of normal olefines: so that no definite conclusion can be drawn from its presence, especially as it is produced to a relatively small extent; in fact, the authors consider that the caproic acid probably owes its origin to the presence of heptylene in the octylene, the separation of the lower olefines by fractional distillation being accomplished with difficulty unless very large quantities of material are dealt with.

It is noteworthy that whereas in the manufacture of oil-gas the paraffins are all but destroyed and no olefine higher than heptylene is obtained, shale-spirit, which is produced by the decomposition of paraffins at a much lower temperature, is rich in paraffins and higher olefines.

67. "The Magnetic Rotatory Power of the Ethyl Salts of Maleic and Citraconic Acids and their Isomers." By W. H. Perkin, Ph.D., F.R.S.

The result of the examination of the ethylic salts of maleic, citra-

conic and itaconic acids show that in the magnetic field they affect polarised light like most substances of the kind differing by 2H from normal saturated compounds.

The author has already shown (*Chem. Soc. Trans.*, 1884, 561) that such unsaturated compounds have a greater molecular rotatory power than saturated compounds to the extent of a little more or less than 1·0; thus, the value for allyl is about 0·914 higher than that of propyl, and the value for oleic compounds is about 1·112 higher than that for corresponding saturated compounds. In the case of the acids under consideration the increase is a little higher still, as the following comparisons show:—

Ethylic maleate	9·647	Ethylic itaconate	10·630
„ succinate. . ..	8·380	„ methylsuccinate	9·347
Difference	1·267	Difference	1·283

Ethylic citraconate	10·499
„ methylsuccinate	9·347
Difference.....	1·152

The small difference between the molecular rotatory power of the itaconic and citraconic salts is undoubtedly due to the structure of the compounds being somewhat dissimilar.

The fumaric and mesaconic compounds afford very considerably higher values, thus:—

Ethylic fumarate ..	10·119	Ethylic mesaconate .	11·269
„ succinate ..	8·380	„ methylsuccinate	9·347
Difference	1·739	Difference	1·922

From these results, maleic, citraconic and itaconic acids may be regarded as ordinary unsaturated compounds related to succinic and methylsuccinic in a similar way that α-crotonic and oleic acids are related to butyric and stearic acids. Fumaric and mesaconic acids belong to a different class of compounds. The interpretation to be given to the very high molecular rotatory powers of these compounds is not at present evident. The results of this investigation do not appear, however, to be in favour of the formulæ lately suggested by Anschutz to explain the isomerism of maleic and fumaric acids.

68. "The Temperatures at which various Sulphates undergo Decomposition." By G. H. Bailey, D.Sc., the Owens College.

On account of the use which is frequently made of sulphates in atomic weight determinations, it is important to ascertain to what temperature they can be heated without undergoing decomposition, as it is necessary to apply heat in order to dehydrate and expel adherent acid. The author heats the sulphate containing excess of acid, in the apparatus which he has previously described, at a known temperature—say 360°—till of constant weight; the temperature is then raised, and the heating continued, &c. For a considerable range of temperature the weight remains constant, but a point is ultimately reached at which further loss of weight occurs, indicating that the temperature has been reached at which the normal sulphate decomposes.

Zinc sulphate begins to decompose at 410°, bismuth sulphate at 405°; lead, magnesium and sodium sulphates are stable up to 500° at least. The behaviour of didymium sulphate is quite different from that of the other salts, and the limits of temperature within which it is stable are not sharply defined.

69. "The Reaction between Sulphites and Nitrites of Metals other than Potassium." By Edward Divers, M.D., F.R.S., and Tamemasa Haga, F.C.S.

Referring to a recent paper by Raschig (*Ber.*, 1887, 584), the authors state that they have for a long time been aware that hydroxylamine is producible from various nitrites by the action of sulphurous acid and sulphites, and have only delayed making this known that they might at the same time communicate the results of their examination of the stages of the reaction when sodium salts are used. Fremy entirely failed to prepare sodium salts corresponding with the potassium compounds he has described. The authors, however, have succeeded in preparing sodium salts which are unmistakably compounds of the simpler acids of which Fremy prepared potassium salts.

On mixing solutions of sodium sulphite and nitrite slight heat is developed (when metasulphite is substituted the rise in temperature is more marked), and the mixture increases in alkalinity; when two formula weights of sulphite to one of nitrite are taken, all sulphite and nitrite, as nearly as possible, cease to exist as such, in about ten days' time. For some time after mixing sulphite can be precipitated as barium salt, nitrite being left in solution; but when the interaction is complete, the barium precipitate is that of a hydroxylamine-sulphonate free from sulphite and sulphate (traces excepted), and the

mother-liquor contains a barium aminesulphonate and very little hydroxylaminesulphonate. On dissolving the barium precipitate in acid, no evidence of the presence of hydroxylamine is obtained until the liquid has been heated: a precipitate of barium sulphate is then produced, much hydroxylamine being then formed. The barium precipitate is probably the slightly soluble salt of hydroxylaminedisulphonic acid, and the soluble barium salt, that of aminetrisulphonic acid, which on heating becomes di- and mono-sulphonic acids, sulphuric acid separating.

By acidifying and heating a mixture of sodium sulphite and nitrite in suitable proportions, the authors have obtained almost all the nitrogen of the nitrite as hydroxylammonium sulphate. Metasulphite appears to be still better suited than the normal sulphite for the preparation of hydroxylamine.

70. "The Action of Acetyl Chloride on Acetoximes." By Victor Meyer and A. W. Warrington, B.Sc.

The authors find that if the acetoxime obtained from isopropylketone and hydroxylamine be treated with acetyl chloride at a low temperature, the corresponding acetate is formed; but that if the temperature be allowed to rise the product is an isomer of the acetoxime. This isomer is a solid, and crystallises in colourless needles; it melts at 102°, and boils at 210°. On hydrolysis it yields isobutyric acid and isopropylamine, and it may be prepared from isobutyric chloride and isopropylamine: an isomeric change therefore takes place, the nature of which may be seen on comparison of the formulæ—

$$\left.\begin{matrix}(CH_3)_2CH\\(CH_3)_2CH\end{matrix}\right\}C:N\cdot OH \qquad\qquad \begin{matrix}CO\cdot CH(CH_3)_2\\|\\NH\cdot CH(CH_3)_2\end{matrix}.$$

Diisopropylacetoxime. Isopropylisobutyramide.

No such isomeric change occurs on similarly treating dipropylacetoxime, the corresponding acetate being the only product.

71. "Sulphinic Compounds of Carbamide and Thiocarbamide." By George McGowan.

The compounds described are—

(1.) $(CSN_2H_4)_2\cdot(Cl_3CSO_2)_2$ = dithiocarbamide ditrichloromethylsulphinate.

(2.) $CSN_2H_4\cdot Cl_3CSO_2H$ = thiocarbamide trichloromethylsulphinate.

(3.) $CON_2H_4\cdot Cl_3CSO_2H$ = carbamide trichloromethylsulphinate.

(4.) $CSN_2H_3\cdot Cl_3CSO_2$ (?) = trichloromethylsulphinylthiocarbamide.

The first of these is prepared from ammonium trichloromethylsulphinate and dithiocarbamide dichloride; the second by dissolving equimolecular proportions of thiocarbamide and ammonium trichloromethylsulphinate in alcohol, and adding a slight excess of a concentrated solution of hydrogen chloride; the third is prepared in the same way as the second, avoiding water, which decomposes it, the fourth is obtained together with dithiocarbamide dichloride by the action of trichloromethylsulphonic chloride on thiocarbamide.

72. "Anacardic Acid." By Dr. S. Ruhemann and S. Skinner, B.A.

Anacardic acid was originally obtained by Staedler from the oil contained in the shell of the fruit of *Anacardium occidentale;* he assigned to it the formula $C_{41}H_{32}O_7$ (C = 6). The authors find that it is an hydroxycarbolic acid of the formula $C_{22}H_{32}O_3$. They describe several salts, and give the results of their analyses.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Ausführliches Lehrbuch der Chemie: Band IV, Th. II: Organische Chemie: von H. E. Roscoe and C. Schorlemmer: Braunschweig, 1887: from the Authors.

The Norwegian North Atlantic Expedition, 1876–1878: XVII. Alcyonida: by D. C. Danielssen: Christiania, 1887: from the Editorial Committee.

Elements of Australian Agriculture: by A. Mackay: Sydney, 1885: from the Author.

A New Basis of Chemistry: by T. Sterry Hunt: Boston, 1887: from the Publisher.

Die Prüfung Chemischer Arzneimittel: von A. Duflos: Breslau, 1866: from Dr. Stevenson.

Chemisches Apothekerbuch: von A. Duflos: Breslau, 1867: from Dr. Stevenson.

Die Chemie der Austrocknenden Oele: von G. J. Mulder: Berlin, 1867: from Dr. Stevenson.

Traité de Chimie Hydrologique: par J. Lefort: Paris, 1873: from Dr. Stevenson.

Guide pour l'Analyse de l'Eau: par E. Reichardt: Traduit par G. E. Strohl: Paris, 1876: from Dr. Stevenson.

California State Mining Bureau: 6th Annual Report of the State Mineralogist, Parts I and II for the Year ending June 1st, 1886: Sacramento, 1886–1887: from the Bureau.

4th Annual Report of the Bureau of Ethnology, 1882–1883: by J. W. Powell: Washington, 1886: from the Smithsonian Institution.

The Chemistry of Tobacco: by J. Bell: London, 1887, two copies: from the Author.

U.S. Geological Survey: Monographs X: Dinocerata: by O. C. Marsh: Washington, 1886: from the Survey.

A Questão dos Vinhos (os Vinhos Falsificados): pelo Campos da Paz: Rio de Janeiro, 1886: from the Author.

II. *By Purchase.*

Anleitung zur Darstellung organischer Präparate: von S. Levy: Stuttgart, 1887.

Le Lait: Études Chimiques et Microbiologiques: par E. Duclaux: Paris, 1887.

Die künstlichen organischen Farbstoffe: von P. Julius: Berlin, 1887.

Kurzes Lehrbuch der organischen Chemie: von A. Bernthsen: Braunschweig, 1887.

HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY, ST. MARTIN'S LANE.

ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 42. Session 1888–89.

November 3rd, 1887. Mr. William Crookes, F.R.S., President, in the Chair.

Sir Benjamin V. S. Brodie, Bart., and Messrs. L. O. Simmons, William Bott and Edward D. Gravill were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Horace Woodward Crowther, Hope Street, West Bromwich; Frank Calder, University College, Bristol; T. Arthur Dickson, 28, Cross Street, Manchester; Charles A. Fawsitt, 4, Maule Terrace, Partick, Glasgow; David Ranken S. Galbraith, Auckland, New Zealand; Joseph C. August Hall, Grosvenor House, Swansea; Casimir James Head, Landore Steel Company, Swansea; James Garnett Heywood, 68, Sutherland Avenue, Maida Vale, N.W.; Walter Hogben, Monville, Seine Inférieure, France; Samuel Lees, Jun., Park Bridge, Ashton-under-Lyne; David Lennox, M.D., 144, Nethergate, Dundee; Eberhard Luttgen, 1814, Mervine Street, Philadelphia, Penna.; Angus Mackay, Sydney, New South Wales; Sidney Martineau, South Road, Clapham Park, S.W.; William Edward Matthews, Kosferd Place, Albert Park, Melbourne; John A. Miller, B.Sc., 16, North Pearl Street, Buffalo, U.S.; John McArthur, 5, Glen Avon Terrace, Partick, Glasgow; John C. H. Mingaye, Taylor Street, Garramatta, Sydney; Archibald R. Ormiston, Heathland, Uddingston; Julius Ostersetzer, Goulding's Chemical Manure Works, Dublin; Andrew William Taylor, Truman Street, Nottingham; Arthur Twivey, 151, Broad Street, Birmingham; José Maria Vargas, 397, Kennington Road, S.E.; John Septibo Ward, 36, Oxford Street, Liverpool Bartlett W. Winder, Sandon Terrace, Sheffield.

The following papers were read:—

73. "Note on the Atomic Weight of Gold." By T. E. Thorpe, F.R.S., and A. P. Laurie.

In a former paper (Trans., 1887, 565) the authors gave as their final result of 25 determinations of the atomic weight of gold the number 196·85, which differs by 0·21 from the value determined by Krüss. Krüss has sought to show, however, that this difference is probably due to the presence of free gold in the bromoaurate of potassium employed by the authors (*Berichte*, 1887, 2365). The authors reply that they were unable to detect any free gold in the salt used by them, and that they therefore altogether dissent from Krüss's conclusion that the lower value of 196·64 is to be preferred.

Discussion.

The President inquired whether the authors had ever attempted to purify the gold by distillation. Stas had stated that it could be volatilised by means of the oxyhydrogen flame, and he had occasion to confirm this observation—in fact, gold boiled violently when heated in a lime crucible by means of the oxyhydrogen blowpipe.

Professor Thorpe replied that no doubt the method suggested might be employed to purify gold. They had obtained their material from the Mint: the only impurity which might have been present was platinum, but it was improbable that it was, as a quantity which might escape detection by qualitative chemical tests appeared to be capable of rendering the gold brittle.

74. "The Interaction of Zinc and Sulphuric Acid." By M. M. Pattison Muir and R. H. Adie.

The experiments described are altogether qualitative. The authors have examined the interaction between sulphuric acid of varying concentration and zinc of different degrees of purity. If pure or nearly pure zinc and moderately dilute sulphuric acid interact at moderate temperatures, they give zinc sulphate and hydrogen only; as temperature and concentration increase the quantity of hydrogen produced decreases, and sulphur dioxide and sulphuretted hydrogen begin to appear. With concentrated acid and nearly pure zinc the chief gaseous product is sulphur dioxide. When commercial zinc is used, sulphur dioxide and sulphuretted hydrogen are produced at almost all temperatures and even with acids as dilute as $H_2SO_4 \cdot 100H_2O$. Zinc sulphate is the only solid product of the interaction at any temperature or concentration of acid. The reaction with platinised zinc-foil resembles that with commercial zinc; in both cases sulphur is formed at moderately high temperatures when

fairly concentrated acids are employed. Variations in the relative mass of zinc employed are without regular influence on the nature of the products of the change. The possible sources of the sulphur and the sulphur compounds are discussed in the light of the tabulated experimental results. The general conclusion is that the interaction between nearly pure zinc and sulphuric acid of different degrees of concentration is chiefly a direct chemical reaction; but that when less pure zinc is employed the reaction is largely electrolytic. The marked influence of concentration and temperature, in every case, makes it probable that the reactions are many and complex, and that they occur between zinc and various molecular aggregates of H_2SO_4 and H_2O, or of H_2SO_4, SO_3 and H_2O.

Discussion.

In answer to Mr. Groves, Mr. Muir said that they had not ascertained whether the sulphur which was produced was the soluble or the insoluble modification.

Replying to Mr. Harcourt he said that they had not attempted to take into direct account the influence of varying amounts of zinc sulphate; he thought, however, that if it had exercised any particular influence this would have been noticed in the course of the experiments, as the conditions had been very greatly varied.

Dr. Armstrong expressed his surprise that the authors should have made in the beginning of their paper a halting confession that interactions such as that between sulphuric acid and zinc were to some extent at least electrolytic; and still more that they should state the opinion that their experiments afforded evidence that in the case of approximately pure zinc "chiefly direct chemical interaction" takes place. It was very remarkable that chemists did not recognise, as physicists had done, that the chemical and electrical phenomena were in such cases absolutely interdependent. The authors had brought forward a large amount of valuable information in their paper, but he could not conceive how any of their evidence could be interpreted as proof of direct chemical interaction—whatever that expression might mean.

In reply to Dr. Armstrong, Mr. Muir stated that by the expression "direct chemical interaction," as compared with the expression used when speaking of the action between sulphuric acid and commercial zinc, viz., "a reaction partly chemical, and also to a large extent electrolytic," the authors meant that in one case zinc, sulphuric acid and water interact in the manner usually called chemical, and that the products are either hydrogen and zinc sulphate, or, with a different concentration of the acid and a different temperature, hydrogen, zinc sulphate and sulphur dioxide; while in the other case,

besides this change, another occurs, viz., the decomposition of the acid by the electric current produced in the chemical reaction occurring between the acid, the zinc and the other metal or metals in the specimen of zinc used. The first change might be, and probably was, electrical as well as chemical; but, if so, the generally used term, "chemical interaction," is here employed to include the electrical as well as the chemical part of the whole occurrence.

75. "Note on Safety Taps." By W. A. Shenstone.

The author has previously pointed out ("Methods of Glass Working," pp. 64–6) that the safety taps recently introduced are open to the rather serious objection that they offer no special resistance to the passage of air in the direction in which leakage is most likely to occur, and that therefore such taps are only trustworthy when employed in conjunction with suitable mercury traps. But it had hitherto escaped his notice, and probably that of others also, that even when so protected these taps are still of unsatisfactory construction, as when the properly lubricated plug of the tap is brought into position the space below the plug remains full of air. If the tap be well made, nearly all this air will remain there during the exhaustion of any vessel that may be attached to either arm of the tap; but afterwards, especially if the lubrication of the tap becomes imperfect, air will gradually find its way from below the plug into any apparatus that may be attached to the tap.

To remove this imperfection a very simple alteration only is required, viz., that the plug shall be drilled so that when the tap is open there is free communication between the space below the plug and the contents of any apparatus of which the tap may form a part.

Discussion.

The President exhibited and described two safety taps, the one sealed in one, the other in two directions, by mercury, which were not open to the objection raised by Mr. Shenstone.

Mr. Shenstone subsequently pointed out that the chance of leakage was very much reduced by placing the two arms of the tap at different levels and bringing them into communication by drilling a hole diagonally through the plug; and he particularly insisted on the importance of this modification of the ordinary method of construction.

76. "Note on Guthrie's Compound of Amylene with Nitrogen Peroxide." By A. K. Miller, Ph.D.

In the examination of the products of the manufacture of oil-gas

(Armstrong and Miller, Trans., 1886, 74) the want of a method of identifying different unsaturated hydrocarbons was keenly felt, and experiments in more than one direction are in progress which it is hoped may lead to a satisfactory solution of the difficulty of analysing complicated hydrocarbon mixtures of a similar nature. It appeared to be not improbable that nitrogen peroxide might prove a valuable reagent for the recognition of some of the constituents, as it was known to combine with certain unsaturated hydrocarbons to form well-defined crystalline derivatives; and it was further hoped that perhaps a reagent might be discovered which would characterise N_2O_4, and might be of service in studying the vexed question of the existence of gaseous N_2O_3. It was conceivable that the formation of crystalline compounds depends on a particular molecular grouping of the carbon and hydrogen atoms, and that they will be producible from a homologous series of like constituted hydrocarbons only and not from their isomerides. A few preliminary experiments only have as yet been made, the work having been postponed from last winter owing to the great difficulty of working with such very volatile hydrocarbons and such comparatively unstable substances in hot weather. The reason for already bringing the subject before the Chemical Society is the recent publication of a paper by Wallach (*Annalen*, **241**, 288), who has to some extent anticipated the author's line of work.

Many years ago, Guthrie (*Annalen*, **119**, 83) showed that when commercial amylene and nitrogen peroxide were brought together, combination took place, the products being a definite crystalline substance, $C_5H_{10}N_2O_4$, which decomposed sharply at 95°, and an oil. Although commercial amylene is known to consist chiefly of trimethylethylene, no proof had been given that Guthrie's compound is derived solely from this hydrocarbon, and not from some other constituent. This being a point of importance in connection with the research as indicated above, pure trimethylethylene was prepared from commercial amylene by agitation with sulphuric acid, &c., according to Wischnegradsky's method (*Annalen*, **190**, 328). The action of pure nitrogen peroxide on trimethylethylene and on the residual amylene was then separately examined. The trimethylethylene, dissolved in either carbon bisulphide or glacial acetic acid and cooled by iced water, was converted almost entirely into Guthrie's crystalline compound; some green oil was also produced, but this crystallised for the most part on standing. On crystallising the product from benzene, prismatic crystals were obtained which decomposed sharply at 99°. No signs of the needles described by Wallach (*loc. cit.*) were observed.

On submitting a small portion of the residual amylene to the

same treatment, no crystals were produced, and on pouring the product into water a separation into three layers was observed. The lowest layer consisted of a heavy oil which could not be made to crystallise by cooling to $-10°$, or by exposure to air. The uppermost layer was very volatile and consisted in all probability of pentane originally present in the amylene.

Experiments were also made with normal amylene and normal hexylene; these both yielded oily products heavier than water, and which also refused to crystallise.

From these results it would appear that trimethylethylene is the only constituent of commercial amylene which yields a crystalline derivative with nitrogen peroxide. It remains to be seen how the remaining isomerides behave.

Discussion.

Professor Dunstan asked whether Dr. Miller had examined the action of reducing agents on Guthrie's compound. He suggested this as a test of the correctness of the formula proposed by Wallach, which represented the compound as a nitrosyl nitrate, a view Victor Meyer had previously rejected, because he obtained all the nitrogen in the form of ammonia by reducing with sodium amalgam. The action of ferrous hydroxide might decide the question, since nitrosyl, if present, would probably yield hyponitrite, while the nitroxyl would be unattacked by the weak reducing agent, and would form amyl nitrate.

Dr. Miller replied that he had not.

77. "The Dehydration of Metallic Hydroxides by Heat, with Special Reference to the Polymerisation of the Oxides and to the Periodic Law." By Professor Carnelley, D.Sc., and Dr. James Walker, University College, Dundee.

The object of this investigation was—*First*, to ascertain whether some light could be thrown on the question of the polymerisation of the metallic oxides (cf. Henry, *Phil. Mag.* [5], **20**, 81) by heating certain hydrates at regularly increasing temperatures, and determining the degree of dehydration thus produced. In this way it seemed probable that data could be obtained for the construction of curves which would indicate whether any compounds were formed intermediate between the normal hydrates and the corresponding oxides, and thus give some information in regard to the general phenomena occurring during the dehydration, whilst the composition of those compounds if formed might also afford some clue to the true

molecular weights of the oxides. *Second*, to determine the minimum temperature of complete dehydration of the metallic hydroxides with a view of ascertaining whether this temperature was a periodic function of the atomic weight of the positive element.

In the paper the methods of working and the full results are given, together with diagrams of curves in which these results are represented graphically. The general conclusions arrived at are as follows:—

1. Precipitated antimony trioxide is anhydrous. On heating it underwent the following changes: Sb_2O_3 or $Sb_{20}O_{30}$ stable up to 360°; then rapid absorption of oxygen with formation of $Sb_{20}O_{32}$ (?); the latter comparatively stable to 415—440°; then further absorption of oxygen with formation of $Sb_{20}O_{35}$ (?); the latter comparatively stable to 500—565°; third absorption of oxygen with formation of Sb_2O_4 or $Sb_{20}O_{40}$; the latter stable from 590° to above 775°.

2. The following definite stable hydrates appear to exist:—

(*a*.) Ag(OH), stable up to about 100°, then rapid loss of water with formation of Ag_2O; the latter stable to 180—270°, then reduction to metallic silver; this reduction complete at 300—340°.

(*b*.) $Hg(OH)_2$, stable up to about 100°; complete dehydration to HgO at about 175°, when incipient decomposition into Hg and O_2 commences, followed by full decomposition at about 415° to 440°.

(*c*.) $CeO_2{\cdot}2H_2O$ or $Ce(OH)_4$ = ortho-ceric hydrate. This hydrate was formed on heating precipitated hydrate of cerium dioxide to about 385°. It remained stable from about 385° to 600°. It was of a light-yellow colour. On heating to over 600°, it underwent dehydration to CeO_2, and became salmon-colonred. This is the only definite stable hydrate of the oxides RO_2 of the silicon-titanium-group obtained. In other respects cerium hydrate on dehydration behaved like the hydrates referred to in § 5.

(*d*.) $5Co_2O_3{\cdot}8H_2O$.—This was the composition of air-dried cobaltic hydrate, and was perfectly stable up to 75°.

3. The following data in regard to the action of heat on the hydrate of Pb_2O will possibly be of interest in the manufacture of red lead:—Hydrate dried in air = $3PbO_2{\cdot}H_2O$; complete dehydration about 230°; PbO_2 stable up to about 280°; loss of oxygen with formation of Pb_2O_3 at 280—290°; Pb_2O_3 stable at 290—360°; loss of oxygen with formation of Pb_3O_4 at 360—415°; Pb_3O_4 stable at 415—530°; loss of oxygen with formation of PbO at 530—580°; PbO stable from 580° to above 815°; PbO fused somewhere between 585° and 630°.

4. Air-dried thallic hydrate = $Tl_2O_3{\cdot}H_2O$, but unstable on heating;

complete dehydration to Tl_2O_3 at about 230°; Tl_2O_3 perfectly stable at 230—360°; reduction to $3Tl_2O_3{\cdot}Tl_2O$ at 360—440°; $3Tl_2O_3{\cdot}Tl_2O$ perfectly stable at 440—565°; rapid loss of oxygen and volatilisation of Tl_2O formed at 585—815°; the rate of loss gradually diminishing after fusion at 630°; remaining Tl_2O_3 constant from 815° upwards.

5. An examination of all the results shows that, with the exceptions referred to in § 2. there was no certain indication of the formation of definite hydrates which were stable through any but possibly a very small range of temperature. From this we must conclude, either that there are no definite hydrates formed on heating at gradually increasing temperatures, or that a very large number of such hydrates are produced under these conditions but are so unstable that a further rise in temperature is sufficient to convert a higher into a lower hydrate. Of these, the second alternative is, for reasons given, by far the more probable.

The results accord entirely with Professor Henry's theory that the known metallic oxides are polymers $n(RO_x)$ of the unknown simple oxides (RO_x). The results also show that in most cases, especially those of SiO_2, TiO_2, SnO_2, Al_2O_3, &c., the cofficient n of polymerisation must be very large, as might be expected from the infusible character of these oxides. Minimum values for this coefficient are indicated in some cases.

6. The retention of water by many oxides at comparatively high temperatures, at and above a red heat, is noteworthy. This is especially interesting in the case of the hydrate $Ce(OH)_4$, which is stable to so high a temperature as 600°. The retention of water at such high temperatures illustrates the great importance in quantitative analysis of the thorough ignition of hydrates before weighing.

7. The minimum temperature of complete dehydration is a periodic function of the atomic weight, as follows:—

(*a.*) *For normal oxides of odd members of the same group, the minimum temperature of complete dehydration diminishes as the atomic weight of the positive element increases.*

(*b.*) *For even members of the same group it increases as the atomic weight of the positive element increases.*

(*c.*) *For normal oxides of elements belonging to the same period the minimum temperature of complete dehydration diminishes from the beginning to the middle, and then increases to the end of the period.*

These results accord with the heats of combination of the normal oxides with water in the formation of hydrates.

8. Of two oxides belonging to the same group, the one which requires the highest temperature for complete dehydration will

usually combine at any other lower temperature with a greater quantity of water per molecule of oxide, though this is not always the case, the pairs SiO_2,SnO_2 and Al_2O_3,In_2O_3 being marked exceptions. From this we may conclude that the order of affinity of the oxides for water is *usually* the same both in *intension* and in *extension*, though not always so.

9. Changes of colour on dehydration which are *permanent on cooling* usually indicate the formation of a definite hydrate, or that the dehydration is complete, or that some other definite chemical change has occurred.

78. "The Bromination of Naphthalene β-Sulphonic Acid." By G. Stallard.

The author has revised and extended the work of Darmstädter and Wichelhaus (*Annalen*, **152**, 303) and Jolin (*Nova Acta Soc. Upsal.*, 1877). He finds that when a strong solution of $C_{10}H_7{\cdot}SO_3K(\beta)$ is acted upon by 1 mol. prop. of bromine, a mixture of mono- and di-bromo-salt is precipitated, consisting chiefly of the former. Their separation is best effected by fractional crystallisation of the copper salts: the mono-salt separates out first in the form of very small pale-green rhombic plates, while the dibromo-salt remains in the mother-liquor, and eventually comes down from a sufficiently concentrated solution in the form of long, sage-green, seaweed-like filaments. The mono-salts examined are the potassium (anhydrous), barium ($+ H_2O$), calcium ($+ H_2O$), sodium ($+ H_2O$)—which all crystallise in colourless needles—and the copper salt ($+ 8H_2O$). The dibromo-salts examined are the potassium ($+ \frac{1}{2}H_2O$), barium ($+ 3\frac{1}{2}H_2O$), calcium ($+ 2H_2O$), and sodium ($+ H_2O$)—which were all obtained in colourless needles—and the zinc salt ($+ 9\frac{1}{2}H_2O$), which separated from solution in the form of a slightly opalescent, almost translucent jelly, and the copper salt ($+ 7H_2O$).

The constitution of these bodies is shown by the fact that the monobromo-salts yield on hydrolysis α-bromonaphthalene, while the dibromo-salts give the so-called β-dibromonaphthalene, which is the $\alpha'\alpha^4$ modification. Hence the tribromonaphthalene (m. p. 86·5°) which Jolin prepared from the dibromo-sodium salt by the action of PBr_5, is either the $\alpha'\beta^2\alpha^4$ or the $\alpha'\beta^{2'}\alpha^4$ modification. The first of these formulæ, however, is inadmissible, since it has been already assigned with good reason to Meldola's tribromonaphthalene of m. p. 114° (*Chem. Soc. Trans.*, 1883, 4) from dibromo-α-naphthylamine, and hence the constitution of the mono- and di-bromo-sulphonic acids above-mentioned must be Br : SO_3H = 1 — 2′ and Br : Br : SO_3H = : 4 — 2′.

Further experiments to test the correctness of this conclusion are in progress. The monobrom-acid appears to correspond to the chlorosulphonic acid which Cleve has recently (*Berichte*, 1887, 72) obtained from nitronaphthalene-β-sulphonic acid.

79. "The Constitution of the three Isomeric Pyrocresols." By W. Bott, Ph.D.

By reducing α-pyrocresol by means of hydrogen iodide, the author has obtained, among other products, a hydrocarbon having the properties of a paraffin and approximately of the composition $C_{15}H_{32}$; zinc-dust appears to reduce pyrocresol in a similar manner—but with difficulty. Attempts to displace the oxygen in pyrocresol by chlorine by means of phosphorus pentachloride were attended with little success—all attempts to purify the product having failed. From these results and those previously obtained by Schwarz and himself, the author draws the conclusion that the pyrocresols are compounds of the type of phenyl ether.

Discussion.

In reply to Dr. Armstrong, who asked why so peculiarly unfortunate a name as "pyrocresols" had been assigned to compounds which were neutral substances and not "ols," *i.e.*, phenols, and could not possibly bear any simple relation to the cresols, Dr. Bott said that he was not responsible for the name; it was selected by Schwarz because they were bye-products of the manufacture of cresols and their homologues, and were obtained when the retorts in which distillation was effected became overheated.

80. "Preliminary Note on certain Products from Teak." By R. Romanis.

The author finds that alcohol extracts a soft resin from teak, but no oil or varnish. On distilling the resin he obtained a crystalline substance which he also found to be present in considerable quantity in the tar resulting from the destructive distillation of teak. The analyses which he has made for the crystals point to the empirical formula C_9H_8O; on oxidation with nitric acid they yield what appears to be a quinone of the formula $C_{18}H_{16}O_2$.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Twenty-third Annual Report on Alkali Works, 1886: by the Chief Inspector: London, 1887: from the Chief Inspector.

The Norwegian North Atlantic Expedition, 1876–1878: XVIII α and β. The North Atlantic Ocean. Its Depths, Temperature and Circulation: by H. Mohn: Christiania, 1887: from the Editorial Committee.

Smithsonian Miscellaneous Collections: XXVIII: Meteorological and Physical Tables: by A. Guyot: XXIX: Catalogue of Scientific Periodicals: by H. Carrington Bolton: XXX: Scientific Writings of Joseph Henry: Washington, 1887: from the Smithsonian Institution.

Mason Science College, Birmingham: Calendar for the Session, 1887–1888: from the College.

Memoranda of Field and other Experiments at Rothamsted: June, 1887: from Sir J. B. Lawes.

Transactions of the Wagner Free Institute of Science of Philadelphia: vol. i, 1887: from the Institute.

Hampshire Field Club: Papers and Proceedings, No. 1, 1887: Southampton, 1887: from the Club.

Exercises in Practical Chemistry: vol. i: Elementary Exercises: by A. G. Vernon Harcourt and H. G. Madan: 4th ed.: Revised by H. G. Madan: Oxford, 1887: from the Editor.

Reports of the Royal College of Chemistry and Researches conducted in the Laboratories, 1845-6-7: London, 1849: from Dr. Hodgkinson.

Timheri: The Journal of the Royal Agricultural and Commercial Society of British Guiana: vol. i; part 1: from the Society.

Mineral Physiology and Physiography: by T. Sterry Hunt: Boston, 1886: from the Author.

A New Basis for Chemistry: by T. Sterry Hunt: Boston, 1887: from the Author.

Practical Organic Chemistry: by J. B. Cohen: London, 1887: from the Author.

Qualitative Chemical Analysis: by C. R. Fresenius: Tenth Edition, translated from the fifteenth German edition: and edited by C. E. Groves: London, 1887: from the Publishers.

Ueber die räumliche Anordnung der Atome in organischen Molekülen: (Pamphlet): J. Wislicenus: Leipzig, 1887: from the Author.

Calendar of the City of London College: For the years 1887-88: from the College.

Handbook of Modern Chemistry, Inorganic and Organic: by C. M. Tidy: 2nd ed.: London, 1887: from the Author.

Elementary Chemistry: by M. M. Pattison Muir and C. Slater: Cambridge, 1887. from the Authors.

Practical Chemistry: by M. M. Pattison Muir and D. Carnegie: Cambridge, 1887: from the Authors.

Notes on the Ancient Iron Industry of Scotland: by W. Ivison Macadam: (Pamphlet): from the Author.

II. *By Purchase.*

Die Berechnungen für Entwurf und Betrieb von Eisenhochöfen: von H. Wedding: Braunschweig, 1887.

Manual of Bacteriology: by E. M. Crookshank: 2nd ed.: London, 1887.

Photography of Bacteria: by E. M. Crookshank: London, 1887.

Untersuchung über Kakao und dessen Prapärate: von P. Zipperer: Hamburg and Leipzig, 1887.

Noveau Dictionnaire de Chimie: par E. Bouant. Fas. I, A—Chaleur: Fas. II, Chalumeau—Goudron: Paris, 1887 (cont.).

Lehrbuch der Zuckerfabrikation: von K. Stammer: 2 Auf: Braunschweig, 1887.

Die Fortschritte in der metallurgischen Probirkunst in den Jahren 1882–1887: von Bruno Kerl: Leipzig, 1887.

Exercises in Quantitative Chemical Analysis with a short Treatise on Gas Analysis: by W. Dittmar: London and Glasgow, 1887.

Heilquellen Analysen für normale Verhältnisse und zur Mineralwasserfabrikation berechnet auf Zehntausend Theile: von F. Raspe; Dresden.

At the next meeting, on November 17th, *there will be a ballot for the election of Fellows*, and the following paper will be read:—

"Experiments on Zinc-copper and Tin-copper Alloys." By A. P. Laurie.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 43. Session 1887–88.

November 17th, 1887. Mr. William Crookes, F.R.S., President, in the Chair.

Messrs. Edwin J. Ball and David Lloyd Howard were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Peter Coulson Burn, Junr., King's Lynn, Norfolk; F. Barker Cooke, 40, Wilson Road, Camberwell, S.E.; Agnew Griffith, Daisy Mount, Blundell Sands, Liverpool; Frank Edward Lease, Caledonia Estate, Province Willesley, Straits Settlements; Edmund George McBretney, 25, Denton Terrace, Castleford, Yorks.; W. Sedgwick Saunders, M.D., 13, Queen Street, Cheapside, E.C.

The following papers were read:—

81. "Zinc-copper and Tin-copper Alloys." By A. P. Laurie.

The author finds that if the zinc plate of a Daniell cell be replaced by a compound plate formed by joining copper and zinc, the cell has the same electromotive force as one in which zinc alone is used; this is true even though the zinc surface be only $\frac{1}{1000}$th part of the copper surface. If the zinc plate be replaced by copper-zinc alloys, no deflection of the electrometer is observed as long as the alloy contains less than 67 per cent. of zinc; at this point, however, a big deflection, practically equivalent to that given by zinc, is suddenly obtained. This result, in the author's opinion, may be taken as evidence of the existence of a compound of the two metals of the formula $CuZn_2$. Alloys containing a greater proportion of zinc behave like zinc alone. Similarly in the case of tin-copper alloys, a sudden rise of electromotive force is observed when the proportion of tin in

the alloy exceeds that which would be contained in a compound of the formula Cu_3Sn. This result is in harmony with the evidence already obtained by observations of the density and thermal and electrical conductivity of the copper-tin alloys. If an alloy containing a larger percentage of tin than Cu_3Sn, in a state of fine division, be placed in a copper cup and used in place of the zinc in a cuprous chloride cell, the excess of tin is gradually eaten out, leaving approximately the alloy Cu_3Sn; this alloy undergoes no change if the circuit be kept closed.

Discussion.

Dr. Wright, after asking whether the author had made any experiments with ternary alloys, referred to observations which he had had occasion to make on lead-zinc-tin alloys. It is well known that lead and zinc will not permanently mix, but that on cooling the lead separates with a little zinc and the zinc with a little lead: he had found that tin behaved itself indifferently to the two metals, dividing itself between them; but the zinc appeared to be able to take up more lead, and the lead more zinc, in presence of the tin.

Mr. Ball said that under Professor Robert Austen's direction he had made experiments on the effect of melting lead—a metal which does not alloy with copper—with copper-tin alloys; it was found, however, that the lead had no influence, the copper-tin alloy separating out unmixed.

Professor Ramsay suggested the application of the author's method to lead-tin alloys, which appeared to be but "solidified solutions."

The President drew attention to the fact that amalgams presented many peculiarities. Thus iron, antimony, sodium, silver and gold will dissolve in mercury; but if antimony amalgam be mixed with sodium amalgam the antimony is thrown out—iron also.

82. "The Halogen Substituted Derivatives of Benzalmalonic Acid." By C. M. Stuart, M.A.

The author describes the preparation of orthochlorobenzaldehyde, orthobromobenzaldehyde and orthiodobenzaldehyde, and their transformation into the corresponding halogen substituted benzalmalonic acids; and the decompositions which these acids and *o*-methoxybenzalmalonic acid undergo when boiled with water: on the one hand (Eq. I), into benzaldehyde and malonic acid; and, on the other (Eq. II), into carbon dioxide and cinnamic acid (see accompanying table; comp. Trans., 1886, 357). On reduction, orthonitrobenzalmalonic acid yields the carbostyrilcarboxylic acid described by Friedlander and Göhring.

	Boiled for 1 hour. Decomposition according to			Boiled for 15 minutes. Decomposition according to		
	Eq. I.	Eq. II.	Total.	Eq. I.	Eq. II.	Total.
Benzalmalonic acid.....	85·8	10·8	96·6	57·8	1·41	59·2
	84·4	10·6	95·0	58·3	1·25	59·5
Orthonitrobenzalmalonic acid.	24·5	5·7	30·2	8·70	1·18	9·88
	23·6	6·5	30·1	8·71	1·25	9·96
	24·4	6·4	30·8	—	—	—
Orthochlorobenzalmalonic acid	65·17	8·40	73·57	30·8	3·36	34·16
	64·35	9·64	73·99	30·8	3·47	34·27
Orthobromobenzalmalonic acid	66·0	10·6	76·6	33·0	3·22	36·22
	67·6	10·2	77·8	32·3	2·84	35·14
Orthiodobenzalmalonic acid ..	67·6	9·09	76·69	33·0	3·5	36·5
	65·7	10·09	75·79	31·9	3·0	34·9
Orthomethoxybenzalmalonic acid.....	78·1	8·16	86·2	45·9	2·72	48·62
	76·4	9·27	85·6	44·0	2·04	46·04

83. "Note on a Modification of Traube's Capillarimeter." By H. S. Elworthy.

The author describes a modification of Traube's instrument for determining fusel oil in spirit by measuring the capillary depression, the essential feature being that the tube is fixed at an angle approaching the horizontal instead of vertical. In Traube's instrument a pure 20 per cent. (by volume) spirit is said to rise 50 mm.; but in the author's modification the rise is 173 mm., and 1 per cent. of fusel oil produces a depression of 25 mm. instead of only 7 mm.

84. "The Formation of Hyponitrites: a Reply." By Edward Divers, M.D., F.R.S.

The paper on the "Formation of Hyponitrites," by Professor Dunstan and Mr. Dymond (Trans., 1887, 646), which I received a few days ago, contains some references to papers by Mr. Haga and myself, and by me alone, which are erroneous, and place us in a false position.

(1.) In the section headed "Discussion of Results," p. 656, the authors say: "We are unable to confirm the statement made by Divers and Haga that ferrous hydroxide in presence of alkali does not form hyponitrite from nitric oxide?" Such a statement has not been made by us. All that we have said on this subject occurs in two lines near the end of a short paper describing the formation of hyponitrite from nitric oxide by acting on it with potassium stannite, in reference to the only experiment we have made with ferrous

hydroxide and nitric oxide, one in which we employed strong solution of potassium hydroxide with the ferrous hydroxide. Our words were (Trans., 1885, 364): "Neither hydroxylamine nor hyponitrite could be detected as products of this reaction." The authors record their repetition of this experiment, with results the same as ours (p. 649), and have thus actually confirmed our only statement in the matter. The authors signally confirm also our other experience with ferrous hydroxide, in failing, like us, *by Zorn's process*, to reduce nitrites and nitrates to hyponitrites.

(2.) The authors find that I regard "the formation of hyponitrites as due to the direct *withdrawal* of oxygen from the nitrite or nitrate by the metal" (p. 657), and give as references my first paper on "Hyponitrites" (*Proc. Roy. Soc.*, 1871), and subsequent communications, more particularly that "On the Production of Hydroxylamine from Nitric Acid," presented to this Society. For the very sufficient reason, however, that I have as yet formed no clear notion of the constitution of hyponitrites, I have never offered any formal theory of their formation, unless it be the very one offered by the authors themselves, incidentally given in my discussion of the reduction of nitric acid by metals (see below). Nowhere otherwise in that paper, nor at all in any other communication, have I treated of the theory of the formation of hyponitrites, so far as I can find. In my first paper occurs only the equation—$NO_2Na + 2Na = NONa + Na_2O$, and the bare statement that the sodium reduces the nitrite. The authors were, therefore, hardly in the position to state that I regard its formation as due to the direct withdrawal of oxygen, the word withdrawal italicised, in order plainly to make a contrast to their supposition that first sodium nitrite directly combines with hydrogen. I have long ago expressed the latter view myself, but I should still express *the result* of the reaction by the above equation in my first paper.

(3.) The authors further find me to suggest "that a compound of the formula $NaNONa_2$ is formed by the *substitution*" (the italics again are theirs), "of two atoms of sodium for one of oxygen in the nitrite $NaNO_2 + 4Na = NaNONa_2 + Na_2O$" (p. 657). But at the place referred to (Trans., 1883, 458), there is only the equation $-Zn(NO)_2 + 4Zn = Zn_2N_2O_2Zn + 2ZnO$, together with words which have rightly led the authors to write 2Na for Zn, and halve the formula. Of the substitution of metal for oxygen there is neither word nor implication in my paper. $Zn_2N_2O_2Zn$, or Na_2NONa, is clearly hydroxylamine with zinc or sodium in place of hydrogen, but the authors have, by some strange error, written, three times over, as my formula, $NaNONa_2$. Such an unjustifiable mode of writing may serve to illustrate the absurd view they attribute to me, that

two atoms of sodium are substituted for one of the atoms of the oxygen of the nitrite (!), but no such view is expressed or countenanced in any paper of mine. The authors will, I am sure, agree with me that a position-formula, which contains two or more groups of atoms of the same element, does not preserve its meaning when rewritten with another arrangement of its symbols.

(4.) Having shown the insufficiency of the views they attribute to me, incorrectly as I have just pointed out, the authors proceed to advance a view of their own, which is nevertheless to be found stated explicitly in that communication of mine to the Society, to which they principally refer. They say: "The hypothesis we wish to suggest as at once the simplest and most in accordance with the facts, supposes that the sodium nitrite first directly combines with two atoms of hydrogen. The formula of the new compound will be $Na{\cdot}N{:}(OH)_2$, or perhaps $NaONH{\cdot}OH$. This substance will on the one hand split up into sodium hyponitrite and water, $2NaN(OH)_2 = Na_2N_2O_2 + 2H_2O$, and on the other be acted on by hydrogen, yielding hydroxylamine and sodium hydroxide, $NaN(OH)_2 + H_2 = NH_2OH + NaOH$. More hydrogen will yield ammonia . . ." (p. 657). Essentially all that is contained in the above extract is given by me in my paper on the "Production of Hydroxylamine from Nitric Acid" (**43**, 443). I there suggest that nitrous acid "passes next to a transition-body capable of decomposing to hyponitrous acid, but readily passing on directly to hydroxylamine, thus: $HNO_2 + H_2 = HN(OH)_2 = HNO + OH_2$, or otherwise, $HN(OH)_2 + 2H = H_2NOH + OH_2$, a repetition of which action would give ammonia" (*op. cit.*, p. 462).

I have much less confidence than the authors appear to have, as to the sufficiency of this view, which was indeed only expressed by me incidentally in connection with the reduction of nitric acid, and I should not have felt induced to assert my claim to it now, had the authors confined themselves to putting it forward as new, and not, with many references to my papers, erred in representing me as having advanced only other and extravagant views.

85. "Reply to the foregoing Note." By W. R. Dunstan.

1. As regards the interaction of nitric oxide and ferrous hydroxide, the statement quoted by Dr. Divers in par. 1, is only a fair interpretation of his own words. If Dr. Divers believed that hyponitrite was formed, but could not be detected in presence of the excess of alkali (which we have shown to be the case), misunderstanding would have been avoided had he explicitly said so, although there would have been at that time an absence of experimental evidence for the

suggestion. This reference to Zorn's process does not correctly represent our conclusion. We found, contrary to the experience of Divers and Haga, that hyponitrite can be formed from nitrite by a process which is substantially that proposed by Zorn.

2. We certainly had gathered from Dr. Divers' papers that he regarded the formation of hyponitrite from nitrite as the result of the direct withdrawal of oxygen by sodium, and not of the intervention of hydrogen. The habitual exclusion of water from his equations is in itself a sufficient justification for our statement. I fail to find in any of Dr. Divers' papers an expression of the view that, in the formation of sodium hyponitrite by the action of sodium on sodium nitrite, water is the necessary link in the series of interacting compounds, and that the hydrogen of this water first attaches itself to sodium nitrite.

3. The "absurd view" that we had attributed to Dr. Divers has arisen from a misunderstanding of his formula Na_2NONa, or, as we had written it, $NaNONa_2$. The equation he gives certainly involves the substitution of sodium for oxygen, but Dr. Divers now explains that the resulting compound is to be regarded not as a sodium-derivative of sodium nitrite, but as a metallic derivative of hydroxylamine.

4. I am surprised to find that Dr. Divers claims as his own the hypothesis we have suggested to account for the formation of hyponitrite and hydroxylamine from nitrites and nitric oxide. He admits that he has never fully discussed the general question. He has proposed a similar theory to account for certain decompositions of nitric acid by the tin-zinc metals, but he nowhere attempts to show that an analogous change takes place when sodium acts on dissolved sodium nitrite. Moreover, there is no recorded evidence that Dr. Divers had noticed the significance of the *simultaneous* formation of hyponitrite and hydroxylamine from sodium and sodium nitrite, and he certainly had not shown that the hydroxylamine was not derived from the hyponitrite; on the contrary, he has suggested that hyponitrite does yield hydroxylamine when hydrogenised (Trans., 1885, 204). It may fairly be said that Dr. Divers was not even in possession of the facts which our hypothesis was devised to explain. My only object in writing this rejoinder is to point out the grounds for attributing to Dr. Divers the views to which he now takes exception. I am glad to find that after all our interpretations of the facts do not appear to be so divergent as I had formerly supposed.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

University College, Nottingham. Calendar for the Seventh Session, 1887-8. Nottingham. 1887. From the Council.

The Chemistry of Nitrogen as disclosed in the Constitution of the Alkaloids, by A. B. Prescott. Salem. 1887. From the Author.

Die Oberharzer Hüttenprocesse zur Gewinnung von Silber, Kupfer, Blei und arseniger Säure, mit besonderer Berücksichtigung des Vorkommens und der Aufbereitung der Erze, von Bruno Kerl. Clausthal. 1860. From Mr. B. H. Brough.

II. *By Purchase.*

Physico-Chemical Constants. Melting and Boiling Point Tables, by T. Carnelley. Vol. II, 4to. London. 1887.

Agriculture in some of its Relations with Chemistry, by F. H. Storer. 2 vols. London. 1887.

The Owen's College Course of Practical Organic Chemistry, by J. B. Cohen. London. 1887.

Laws and Definitions connected with Chemistry and Heat, with explanatory Notes on Physical and Theoretical Chemistry, also Special Tests and Examples for Practical Analysis, by R. G. Durrant. London. 1887.

Le potential thermodynamique et ses applications à la mécanique chimique et à l'etude des phénomènes électriques, par P. Duhem. Paris. 1886.

At the next meeting, on December 1st, *there will be a ballot for the election of Fellows*, and the following papers will be read:—

"The alleged Existence of a Third Nitroethane." By Professor Dunstan and T. S. Dymond.

"An Extension of Mendeleeff's Theory of Solution." By Holland Crompton.

"Note on Electrolytic Conduction and on Evidence of a Change in the Constitution of Water." By Professor Armstrong.

"Researches on the Laws of Substitution in the Naphthalene Series." By Professor Armstrong.

RESEARCH FUND.

A meeting of the Research Fund Committee will be held in December. Fellows desiring grants are requested to make application before December 12th.

NOTICE TO AUTHORS OF PAPERS.

To facilitate the preparation of the abstract accounts of the Proceedings at the meetings of the Society, all authors are requested to furnish abstracts of their communications, and to send their papers so that they may be in the hands of the Secretaries, if possible, on the Monday before the day of meeting. Authors are also requested to write on their papers *the address to which they wish proofs to be sent.*

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 44. Session 1887–88.

December 1st, 1887. Mr. William Crookes, F.R.S., President, in the Chair.

Mr. Henry Droop Richmond was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Edward Arthur Andrews, 52, Camden Road, N.W.; Albert Wodehouse Day, Lancing College; Philip Anderson Estcourt, Vyrniew House, Talbot Road, Old Trafford, Manchester; William Gay Forsyth, 2, Granville Place, Glasgow; John Booth Kirkland, Prince's Hill, Carlton, Melbourne; Thomas Atkinson Lawson, Ph.D., B.Sc., 15, Alexandra Road, N.W.; Frederick William Shaw, Heapey Bleach Works, North Chorley.

The following were elected Fellows of the Society:—Messrs. Frank Calder, Horace Woodward Crowther, T. Arthur Dickson, Charles A. Fawsitt, David R. S. Galbraith, Joseph C. A. Hall, James G. Heywood, Cassimir J. Head, Walter Hogbin, Samuel Lees, jun., David Lennox, Eberhard Luttgen, John McArthur, Angus Mackay, Sydney Martineau, William E. Matthews, John A. Miller, B.Sc., John C. H. Mingaye, Archibald R. Ormiston, Julius Ostersetzer, Andrew W. Taylor, Jose Maria Vargas, John Septibo Ward, Bartlett W. Winder.

The following papers were read:—

86. "The Alleged Existence of a Second Nitroethane." By W. R. Dunstan and T. S. Dymond.

The authors have repeated the experiments of Kissel (*Jour. Russ. Phys. Chem. Soc.*, 1882, 226—230; and 1884, 135—140), who alleges that when the interaction of ethyl iodide and dry silver nitrite takes

place at 0°, no ethyl nitrite is formed, but nitroethane, together with a new isomeride (b. p. 29—30°), which though possessing certain of the properties of ethyl nitrite appears to be more closely allied to nitroethane. The authors were unable to isolate any such substance. They show that by carefully fractionating the liquid obtained from the interaction at 0° of ethyl iodide and dry silver nitrite, it may ultimately be resolved into ethyl nitrite and nitroethane, and further, that fractions which distil at low temperatures (below 100°) exhibit the chemical properties of a solution of ethyl nitrite in nitroethane.

87. "An Extension of Mendeléeff's Theory of Solution to the Discussion of the Electrical Conductivity of Aqueous Solutions." By Holland Crompton.

The method made use of by Mendeléeff in his paper on "The Compounds of Ethyl Alcohol with Water" (*Chem. Soc. Trans.*, 1887, 778), in which the dependence of change of relative density on percentage composition was considered, has been applied by the author, at Dr. Armstrong's suggestion, to the discussion of the electrical conductivity of aqueous solutions, the determinations given by F. and W. Kohlrausch being made use of for the purpose.

The curve obtained in the case of sulphuric acid, representing change of conductivity with percentage composition $\frac{dk}{dp}$ as depending on the conductivity, was not found to give evidence of the presence of any hydrates in solution. A second differentiation was therefore resorted to and the coefficient $\frac{d^2k}{dp^2}$ plotted out for different percentage compositions. The curve thus obtained has an undoubted rectilinear character and is discontinuous, having breaks at points corresponding to hydrates of the composition $H_2SO_4{\cdot}OH_2$, $H_2SO_4{\cdot}2OH_2$, $H_2SO_4{\cdot}6OH_2$, $H_2SO_4{\cdot}24OH_2$, and $H_2SO_4{\cdot}150OH_2$. The presence of all these hydrates, with the exception of that with 24 molecules of water, in aqueous solutions of sulphuric acid has already been recognised by Mendeléeff, who deduced their existence by discussing the change in density of such solutions by the same method that he employed in the case of ethyl alcohol. It is concluded from this that the electrical conductivity of sulphuric acid solutions cannot be a continuous function of the percentage composition, but that it is influenced by certain hydrates existing in the solution, indication of the presence of which is afforded by the second differential coefficient curve.

A certain irregularity exists at each end of the second differential coefficient curve, where the pure compound may be said to first undergo dilution. This is regarded as representing an initiative

stage during which the action of the compounds just beginning to be formed has not come fully into play and the conductivity is influenced by a number of physical actions here probably taking place. It is also pointed out that no break occurs on the second differential coefficient curve corresponding with the maxima observed on the conductivity curve, as the maxima are found to occur at points intermediate between the breaks on the second differential curve. The influence of both hydrates present on the conductivity seems to determine the maximum, which probably represents that the sum of the influence of each is here greatest.

Further confirmation of these facts is obtained by the discussion of other solutions, all of which are found to act in a manner similar to sulphuric acid. In the case of nitric acid there is evidence of the formation of two hydrates, $HNO_3 \cdot 15OH_2$ and $HNO_3 \cdot 4OH_2$; and in that of phosphoric acid of the two hydrates $H_3PO_4 \cdot 8OH_2$ and $H_3PO_4 \cdot 2OH_2$, the presence of the same hydrates being also indicated in each case by Mendeléeff's curve for change of density. In the case of potassium and sodium hydroxides, the hydrates appear to be the same, namely, one with 10, and one with 6 molecules of water.

The fact that the second differential coefficient is a rectilinear function is regarded as evidence that the conductivity is a function of the third order of the percentage composition, $K = A + Bp + Cp^2 + Dp$, this function, however, being only continuous between the limits indicated.

88. "Note on Electrolytic Conduction and on Evidence of a Change in the Constitution of Water." By Henry E. Armstrong.

In this addendum to the foregoing paper, the author claims the results in support of the hypothesis which he has elsewhere advocated that electrolysis is not a mere dissociation phenomenon but depends on an influence which one set of molecules exerts on another set while both are under the influence of the electromotive force. Discussing the first differential coefficient curve, he points out that the influence is exerted almost entirely at two points: in the interval between the acid and the hydrates $H_2SO_4 \cdot OH_2$ and $H_2SO_4 \cdot 2OH_2$; and especially in the interval between the two hydrates $H_2SO_4 \cdot 6OH_2$ and $H_2SO_4 \cdot 24OH_2$. It is suggested that the comparative smallness of the effect in the former case is due to the acid being present in a "polymerised" less active state, and that the lower hydrates are perhaps also derivatives of a polymer of H_2SO_4. Indication is afforded by a break in the curve of the existence of a compound $2H_2SO_4 \cdot SO_3$. The author is informed by Dr. Messel that on mixing the anhydride and acid, crystallisation first takes place when the mixture has about the com-

position of such a compound, thus confirming its existence. It is suggested that peculiar breaks in the curve when a small percentage of acid is present with the water, or *vice versâ* are evidence of a change in the molecular composition of the fluids. Lastly, it is suggested that the electrolysis of fused salts may be supposed to take place in the same way as that of solutions, *i.e.*, that they contain molecules of different orders of complexity capable of influencing each other, and that it is no longer necessary to suppose that there is any fundamental difference in the mode in which the two classes of electrolytes are affected.

Discussion.

The President remarked that the results obtained by Mendeléeff, and now by Mr. Crompton, illustrated the necessity of caution in drawing conclusions from curves which directly represented the results of observation.

Mr. Pickering characterised Mendeléeff's recent communications on density curves as containing a discovery of the highest importance. The acceptance of the hypothesis involved in his conclusions must depend on whether the breaks shown by the differential curves occurred at points exactly corresponding to hydrates of definite composition, and whether different physical properties of the same solution all exhibited breaks at the same points. Mr. Crompton's investigation afforded the first evidence that this latter confirmation was forthcoming. For some months past Mr. Pickering had been examining the curves representing the densities, specific heats and heat of dilution of salt solutions, and he felt confident that the results would confirm Mendeléeff's views and afford conclusive proof as to the chemical nature of dissolution. He intended also to further examine the heat of dilution of sulphuric acid, and from the heat of dilution he hoped to obtain more definite results than from the study of densities. As far as his present results went, he had obtained evidence in two or three cases of breaks at about $150H_2O$, as well as breaks at a much higher state of dilution. He did not, however, believe in the existence of compounds such as cryohydrates were assumed to be, and thought that such breaks might well be explained, as Dr. Armstrong suggested, on the view that water and liquids in general were made up of molecular aggregates.

Dr. Morley agreed with Professor Pickering that it was much better to make the curves tell their own story in the manner indicated by Mr. Crompton and Dr. Armstrong, than to divide them by the eye into arbitrary sections in the way which had hitherto been usual. He anticipated that the new method would lead to important results. At the same time he did not quite see at what point differentiation

should stop: Mendeléeff had differentiated his curves once, Mr. Crompton had performed the operation a second time—why should it not be executed a third or a fourth time? It was obvious that the position of the maxima and minima was greatly changed after each differentiation, and therefore the system of straight lines which most nearly approximated to the curve would be different in each case.

No doubt, if at any time the curve should exactly resolve itself into straight lines that would be a proper time to stop, but, if only on account of experimental errors, it was not likely that this would often happen. If we knew the law that governed the change of conductivity of a solution whose molecular constitution was not altered by dilution, the problem would be solved; thus if the curve expressing that law were a conic section we should differentiate once, if it be a cubic we must differentiate twice, and so on. For example, the same experimental curve might perhaps be represented, within the limits of experimental error, either by portions of five conic sections, by portions of three cubics, or by parts of two curves of the fourth degree; which representation was to be chosen?

Professor Ramsay agreed with Dr. Morley's remarks. He asked Mr. Crompton whether any physical meaning was to be attached to the second differential coefficient, or if it was merely found to fit the facts. Commenting on Dr. Armstrong's remarks, he asked to be informed what special views on electrolysis were held by Dr. Armstrong which could be supported by the proof of the existence of complex molecular aggregates. Dr. Armstrong had spoken of such molecular aggregates being urged past each other by the electric current; but of this there would appear to be no proof, for as far as the speaker knew, there was no proof of the separation of such aggregates to opposite poles during the passage of a current. Moreover, granting Dr. Armstrong's assertion that such transference of molecular aggregates in opposite directions did occur, how is the fact of electrolysis to be explained by the friction of those travelling in opposite directions? Did Dr. Armstrong imagine that the corners of such aggregates were rubbed off?

Mr. Crompton, replying to Dr. Morley's objection that there did not seem to be any reason why a limit should be put to the differentiation when that operation had been performed twice, and that it would be just as reasonable to proceed with a third or fourth differentiation and so on, said that a limit to the differentiation would necessarily have to be made according to the nature of the case under investigation and the discretion exercised by the investigator. In the present instance the limit of differentiation is clearly indicated by the agreement of the results obtained with those previously arrived at by Mendeléef by discussing a totally different physical property. There

would obviously be nothing gained by a further differentiation in the present case, for supposing that operation to be again performed, it would give first a constant, and on repetition zero, or at most leave the errors due to experiment, and those which come in when performing the differentiation. In general it is easy to recognise when this stage is reached, provided that the errors are small, as in the experiments under discussion. In reply to Professor Ramsay he said that he could not give any physical meaning to the second differential coefficient.

Dr. Armstrong said that he could not now usefully reply to the questions put by Professor Ramsay, as to do so would involve a lengthy explanation of all that had previously been urged; moreover his views had been fully stated in documents which were in the hands of the members of the British Association Electrolysis Committee.

89. "Bismuth Iodide and Bismuth Fluoride." By B. S. Gott and M. M. Pattison Muir.

The preparation of bismuth iodide in the wet way, by addition of potassium iodide to a solution of bismuth nitrate, is described. The amounts of decomposition of specimens of bismuth iodide prepared in the wet and dry ways by heating with water are tabulated, and shown to be practically the same.

The preparation of bismuth fluoride by adding potassium fluoride solution to a solution of bismuth nitrate, is described, and the properties of this salt are enumerated.

The relative densities of BiI_3, BiF_3 and BiOF are given.

90. "The Action of Hydrogen Sulphide on Arsenic Acid." By B. Branner, Ph.D., and F. Tomiček.

When arsenic acid is treated with hydrogen sulphide, the precipitate consists either of arsenic pentasulphide or contains in addition arsenic trisulphide and sulphur. The author's find—(1) that when a *rapid* current of hydrogen sulphide is passed into a warm solution of arsenic acid containing chlorhydric acid, the pentasulphide is formed slowly, but completely: $2H_3AsO_4 + 5H_2S = As_2S_5 + 8H_2O$; (2) that in solutions of the acid, or when the gas is passed *slowly* into warm solutions of arsenates containing chlorhydric acid, a secondary reaction takes place together with the first chief reaction, but never alone, viz.: (*a*) $H_3AsO_4 + H_2S = H_3AsO_3 + S + H_2O$; (*b*) $2H_3AsO_3 + 3H_2S = As_2S_3 + 6H_2O$.

91. "Note on the Constitution of Mairogallol." By C. S. S. Webster.

On chlorinating the trihydric phenols pyrogallol and phloroglucinol,

I succeeded in obtaining from both the trichloro-derivative (*Chem. Soc. Trans.*, 1886, 423), this stage of the chlorination having previously been overlooked in both cases. Identical results have since been published, without the slightest reference to my work, by K. Hazura and Benedikt (*Chem. Soc. Abstr.*, 1886, 52), and by A. Hantzsch and K. Schniter (*Ber.*, **20**, 2033—2040).

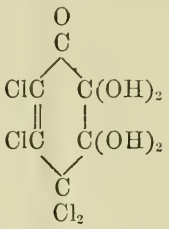
The continued action of the halogen operates very differently on the two trichloro-derivatives: in the case of phloroglucinol the benzene nucleus is broken down and chloracetic acids are formed; in the case of pyrogallol there is a union of the C_6 nuclei with formation of C_{18} derivatives, though from the empirical composition of these it can scarcely be doubted that the double union of the carbon-atoms is resolved at several points. Since the publication of my last note I had been engaged in investigations into the constitution of mairogallol and leucogallol, the C_{18} derivatives in question, the results of which have now to a certain extent been anticipated by Hantzsch and Schniter. Their discussion of the constitution of these compounds is based upon one observation only, viz., that they yield trichloropyrogallol as the chief product on reduction by zinc and sulphuric acid. From this and the numerical ratios of the empirical formulæ they arrive at a constitutional formula representing them as a species of quinone-chlorides.

The decompositions, which I had studied with the object of elucidating their constitution, are those by water, by heating alone, and by the action of the hyposulphites. On boiling mairogallol with water, a rapid decomposition sets in, carbonic anhydride is liberated, and the residual products in solution are oxalic acid and trichloropyrogallol. If sulphurous acid be introduced during the heating, a similar decomposition ensues, but the solution contains in addition to the above-named products a condensed derivative, which is precipitated from solution by gelatin. On treating mairogallol with sodium hydrogen sulphite in aqueous solution and adding zinc-dust, reduction ensues; the chief product is again trichloropyrogallol. In addition to this, amorphous substances are obtained, which may be separated by precipitation with lead acetate and subsequently purified; these resemble the lignocelluloses in giving furfural on distillation with dilute sulphuric acid, and yellow-coloured substitution-derivatives with chlorine, characterised by the magenta reaction with sodium sulphite. On gradually heating mairogallol a sublimate of trichloroquinone and tetrachloroquine is obtained. The residue is a mixture of a number of products, some of which were isolated in the crystalline form, but in quantity too minute for investigation. Some are amorphous, and precipitated by gelatin from aqueous solution.

Leucogallol when heated at 100° is easily converted into trichloro-

pyrogallol and a product reacting like quinone. Following up the indications of these results, I endeavoured to obtain synthetical products from quinone (chloroquinones) and trichloropyrogallol, but I could obtain no products of combination.

These results undoubtedly confirm the view of Hantzsch and Schniter, that the compounds in question are derived by condensation from a hypothetical molecule represented by the formula—



a substituted quinone in which one of the characteristic oxygens is displaced by Cl_2 and the aromatic linking of the carbon-atoms in part resolved.

It is well, however, to bear in mind that this view is based rather upon inferences from the empirical formula than upon actual proof; and it is at least probable that one or more of the C_6 nuclei are more completely resolved, in respect of aromatic constitution, than has been assumed.

With the view of further elucidating the matter, I was engaged at the time of the publication of the paper in question, and still am, in studying these decompositions quantitatively.

In the course of this investigation I had occasion to recrystallise mairogallol from chloroform. Two specimens obtained in this way, after drying at 100°, gave on analysis 52·41 and 52·47 Cl per cent. respectively, whereas a specimen recrystallised from benzene gave 30·34 per cent. Cl (calc. $C_{18}H_7Cl_{11}O_{19}$ = 50·4 per cent. Cl); (calc. $3_{18}H_7Cl_{11}O_{10} \cdot CHCl_3$ = 52·37 per cent. Cl). The chloroform appears, therefore, to be retained in molecular combination.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Presented by Sir Henry E. Roscoe.

Chemistry, by the late G. Wilson, revised and enlarged by Stevenson Macadam. London and Edinburgh.

Arithmetical Chemistry or Arithmetical Exercises for Chemical Students, by C. J. Woodward. Part II. London 1883.

The Owens College Course of Practical Chemistry, by H. E. Roscoe and F. Jones. London 1872.

Twenty Lessons in Inorganic Chemistry, by W. G. Valentin. London and Glasgow 1879.

Analytical Chemistry, by W. Dittmar. London and Edinburgh 1879.

Practical Chemistry: The Principles of Qualitative Analysis, by W. A. Tilden. London 1880.

The Harveian Oration delivered at the Royal College of Physicians October 18th, 1886, by F. W. Pavy. London 1886.

Questions on Physics, by S. Young. London 1887.

Expansion of Structures by Heat, by J. Keily. London 1887.

First Grade Inorganic Chemistry, by T. Ward. Manchester.

Practical Chemistry, by S. Macadam. London and Edinburgh.

Počátové Chemie, sepsal V. Safařik. Praze 1884.

Recherches scientifiques et publications diverses, par F. Kuhlmann. Paris 1877.

Le livre des parfums, par E. Rimmel. Paris.

Die Spectralanalyse in einer Reihe von sechs Vorlesungen mit wissenschaftlichen Nachtragen, von H. E. Roscoe. Autorisirte deutsche Ausgabe bearbeitet von C. Schorlemmer. 2te Auf. Braunschweig 1873.

Fabriques de produits chimiques. Rapport à M. le Ministre de l'Intérieur, par la Commission d'Enquête. Bruxelles 1856.

The Chemical News. Vols. 1-14, 17-20. 1860–1866, 1868–1869.

Société chimique de Paris. Répertoire de Chimie pure, par A. Wurtz et F. Le Blanc. 4 tomes. Paris 1858–62.

——————————— Répertoire de Chimie appliquée, par C. Barreswill. 5 tomes. Paris 1858–63.

——————————— Bulletin des séances. Paris 1863.

——————————— Nouvelle série. Tomes 2, 3. Paris 1864.

Exposition Universelle Internationale de 1878. Rapports du Jury International. Introduction. Classes 4, 5, 7, 9, 12, 13, 15, 16, 19–28, 30–33, 35–42, 43 i and iii, 44, 46–51, planches 51, 54–65, 67, 69–73, 75, 77, 78, 80, 83–85, 87, 89. Paris 1880–83.

Report of Her Majesty's Commissioners for the Paris International Exhibition of 1878. 2 vols. London 1880.

Exposition International d'Électricité. L'électricité et ses applications. Expose sommaire et notices sur les différentes classes de l'exposition. Paris 1880.

Papers read before the New Orleans Academy of Sciences 1886-1887, vol. i, part 1. New Orleans 1887. From the Academy.

Dyeing and Tissue-printing, by W. Crookes, F.R.S. London 1882. From the Author.

At the next meeting, on December 15th, the following papers will be read:—

"An Apparatus for Comparison of Colour Tints." By A. W. Stokes.

"The Sulphonation of Naphthalene." By Dr. Armstrong and W. P. Wynne, B.Sc.

"Isomeric Change in the Naphthalene Series. Nos. 1, 2, 3 and 4." By Dr. Armstrong and Messrs. Amphlett, Williamson and Wynne.

"Notes from the Chemical Laboratory of the Yorkshire College of Science. (1.) The Reduction of Chlorates by the Copper-zinc Couple. (2.) The Oxidation of Oxalic Acid by Potassium Bichromate. (3.) A Method of Separating Supernatant Liquids." By C. H. Bothamley.

"The Alloys of Copper and Antimony and of Copper and Tin." By E. J. Ball, Ph.D.

RESEARCH FUND.

A meeting of the Research Fund Committee will be held in December. Fellows desiring grants are requested to make application before December 12th.

NOTICE TO AUTHORS OF PAPERS.

To facilitate the preparation of the abstract accounts of the Proceedings at the meetings of the Society, all authors are requested to furnish abstracts of their communications, and to send their papers so that they may be in the hands of the Secretaries, if possible, on the Monday before the day of meeting. Authors are also requested to write on their papers *the address to which they wish proofs to be sent.*

HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY, ST. MARTIN'S LANE.

ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 45. Session 1887–88.

December 15th, 1887. Mr. William Crookes, F.R.S., President, in the Chair.

Messrs. Herbert E. Kirby, John Norman Collie and Sydney Martineau were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Samuel Banner, Sherwood, Sefton Park, Liverpool; Arthur G. Bloxam, Royal Agricultural College, Cirencester; Lewis Walter Hawkins, 18, Burr Street, London, E.; Stevenson J. C. G. Macadam, Brighton House, Portobello, Edinburgh; Sidney Skinner, B.A., Christ's College, Cambridge; Charles Francis Townsend, Ashley Road, Epsom; Alfred Edwin Tutton, 12, South Parade, Brompton, S.W.

The following papers were read:—

92. "An Apparatus for Comparison of Colour-tints." By Alfred W. Stokes.

In operations such as Nesslerising in water analysis, when it is necessary to compare a number of depths of tint with one another, it is very inconvenient to have to make up a large series of standard tints. The author has devised an apparatus which obviates this necessity. It consists of a base-board on which lies a sheet of white opal glass. Placed obliquely a little way above this is a sheet of glass on which rest the Nessler-tubes containing the solutions whose tints are to be compared. The mouth-ends of these tubes recline in grooves hollowed in a horizontal bar. This bar is supported by two pillars, on one of which slides a ring clasping a calibrated glass tube: this tube has a side tubulure at the base, and is thus and by means of a short india-rubber tube connected with a similar but uncalibrated

tube resting on the glass plate. A known quantity of the standard colour being placed in the tube carried by the ring and diluted up to the top mark with water, if the movable tube be raised, this standard solution will flow into the tube resting on the glass plate. The movable tube is calibrated to show how much is present in the other tube. Hence, if a Nessler-tube containing liquid of unknown depth of tint be placed beside the tube on the glass plate, and the tube in the sliding ring be raised or lowered till the tints agree in the two tubes resting on the glass plate, a simple inspection of the level of the liquid in the calibrated tube will give the quantity of standard colour the unknown solution is equal to.

The apparatus is especially useful in Nesslerising; also in determinations of the quantity of lead present in waters; and in other cases where comparison of tint depths is necessary.

93. "The Alloys of Copper and Antimony and of Copper and Tin." By E. J. Ball, Ph.D.

The author gives the results of experiments instituted with the view of obtaining further evidence as to whether the alloys Cu_2Sb and Cu_4Sb, which are indicated by changes in the direction of the curve by which the electrical conductivity of the copper-antimony alloys is expressed, are or are not compounds. Copper, antimony and lead were melted together in varying proportions, lead being a metal which alloys only to a very slight extent with copper. Mixtures of Cu_2Sb and lead were first made, the first alloy containing 95 per cent. of lead; the second 90 per cent. of lead; and so on for the remainder of the series. No alloys could be formed between the one with 20 per cent. and that with 65 per cent. of Cu_2Sb. The intermediate mixtures that had separated on solidification were all melted up together and allowed to cool slowly, with the result that owing to the partial oxidation and consequent loss of antimony in the successive fusions and castings, the metal was found to have separated on solidification into three alloys of different densities. The upper of these had the composition Cu_4Sb, the alloy which occupies the lowest position on the conductivity curve. The mixture of 75 lead and 25 Cu_2Sb, the first that separated after fusion, when cast in a cylindrical mould, separated on cooling into two concentric cylinders the inner of which had the same composition as that of the last alloy that formed before the separation of the fused mixture into two alloys, *i.e.*, 80 lead and 20 Cu_2Sb. The author is of opinion that this represents the saturated solution of Cu_2Sb in lead. The alloys were then cast into discs, which were ground to the same size and examined by the aid of the Hughes' induction balance. The curve of relative conductivity so

obtained was practically a straight line between the terminal points. In view of this fact, and since in their general appearance the alloys resemble both in colour and structure mixtures of Cu_2Sb and lead, it would appear that Cu_2Sb exists in these alloys as such.

In the second series of alloys, the first mixture consisted of 95 antimony, 2·5 lead and 2·5 copper; the second of 90 antimony, 5 lead and 5 copper. These alloys were all more or less grey in colour, and their fracture became conchoidal as the alloy approached in composition Cu_4Sb. The induction balance curve rose gradually, till the copper and antimony were almost in the proportions necessary to form Cu_2Sb, and then fell again as this point was passed.

In the third series, the first alloy formed contained 95 copper, 2·5 lead and 2·5 antimony; the second contained 90 copper, 5 lead and 5 of antimony. All the alloys of this series formed, except the one with 50 copper, 25 lead and 25 antimony; this separated on cooling into an alloy which was again found to have the composition Cu_4Sb and lead containing antimony and copper. The induction balance curve of this series, allowing for the dilution of the copper-antimony alloys by lead, is identical with that of the copper-antimony alloys free from lead. Throughout these three series of alloys the lead appears to be wholly without influence on the physical properties except that which it exercises as a diluent, the influence of the alloys forming the turning points of the conductivity curve, Cu_2Sb and Cu_4Sb, being as marked in the presence of lead as when that metal is absent. Hence the author believes that these two alloys are true compounds. When they are fused with silver sulphide, the copper in both Cu_2Sb and Cu_4Sb is to a great extent displaced by silver, without greatly altering the character of the alloy.

Copper-tin alloys were treated with lead in a similar manner, and in this case also the lead appeared to be without effect on the general character of the alloys, the influence of the alloys which are indicated by the turning points of the conductivity curve, viz., Cu_3Sn and Cu_4Sn, being as marked as in the case of the turning points of the copper-antimony alloys Cu_2Sb and Cu_4Sb.

Discussion.

Professor Roberts-Austen said that the alloy of copper and antimony known as the "Regulus of Venus" is the only alloy having an intense violet colour, which made it an object of great interest to the alchemists, but it had been strangely neglected by their successors in modern times. Lead unites readily with antimony, and it therefore appeared not improbable that lead would induce a certain amount of antimony to leave the copper and form triple alloys; but Dr. Ball had

shown that the antimony and copper alloys remained intact, and that lead merely diluted them. This was specially interesting because, to turn to other metals, it is well known that zinc and lead if melted and mixed in the fused state separate from each other almost entirely on cooling. Notwithstanding this fact, A. and L. Svanberg had shown that in the presence of a third metal, viz., tin, lead and zinc will unite to form a triple alloy $ZnSn_3 + 2PbSn_3$, which solidifies at 168° C. It was generally assumed that rapid cooling prevented the "liquation" or separation of the constituents of alloys, but the speaker had shown in the case of the silver-copper alloys, that *slow* cooling produced products as uniform in composition as Levol's alloy containing 71·8 per cent. of silver, the only alloy of the series which was formerly believed to be uniform in composition.

Professor Roberts-Austen added that he was glad of the new evidence afforded by the author's observations of the delicacy of the Hughes induction balance, an instrument which he had long since predicted would prove to be of great service in studying the molecular constitution of alloys.

Dr. C. R. Alder Wright said that the determination of the constitution of ternary alloys involved the solution of some very interesting problems, which in certain cases appeared to be of a far more complex order than was generally supposed. A great distinction was to be made between the amount of permanent miscibility possible with fluid metals whilst kept molten by heat, and the more or less complete segregation taking place during solidification on cooling, especially when slowly effected. In the latter case the separation appeared frequently to be regulated by the formation of alloys of definite constant compositions, atomic or otherwise, which possessed fusing points higher or lower than those of the rest of the masses: so that one portion solidified first, leaving, so to speak, a more fusible mother-liquor. But it was quite different in the former case: with certain metals in certain proportions the mixture when melted, well stirred together and then left quiescent for some time in a molten condition, separated into two layers, just as a mixture of ether and water, or certain mixtures of ether, alcohol and water would do if shaken up and then allowed to stand; the relative proportions in which the metals divided themselves were doubtless regulated by some law, because one given mass always divided itself in one way, and another in another, and so on; but this law or guiding principle did not seem to be connected with combination in atomic proportions, nor upon the production of any one particular alloy which formed and separated from the rest of the mass. He was not in a position at present to indicate what really was the guiding principle in such cases, but hoped that some experiments upon which he and Mr. C.

Thompson were now engaged would throw light on the question. These experiments were being carried out with various mixtures of lead, zinc and tin or bismuth: thus for example a series of ingots were made by mixing equal weights of lead and zinc in each case with varying amounts of tin, melting together, well stirring and keeping molten for one to two hours, and then cooling without more delay than was absolutely necessary in order to diminish possible sources of error through incipient segregation during solidification taking place in either the bottom or the top one of the two layers into which the molten mass divided itself during the period of quiescence. The top and bottom portions being analysed and the lead and tin calculated per unit of zinc in the first case, and the zinc and tin per unit of lead in the second, and these pairs of values being plotted off as abscissæ and ordinates respectively, curves were obtainable from comparison of which he hoped to be able to deduce the guiding principle. In each case the amount of zinc taken up by the heavier alloy in which lead predominated, and that of lead in the lighter alloy in which zinc predominated, increased with the amount of tin present; but not always in the same ratio. Moreover, the relative proportions in which the tin divided itself between the bottom and top layers was not constant, but varied with the proportion of tin in the total mass; so that the production of atomic compounds of the metals, even if it occurred at all, was certainly not the sole explanation of the results. The principle of two saturated solutions being formed also appeared to be inapplicable.

In answer to a further question by Dr. Ball, Dr. Alder Wright said that his experiments were as yet hardly complete enough to enable him to pronounce definitely, but he thought that the formation of an eutectic alloy would not afford an adequate explanation, because if this were the case, either the top or the bottom layer (presumably the latter, being usually the more fusible) should exhibit constancy of composition which was very far from being the case; the principle of eutexia no doubt largely regulated the solidification of molten masses on cooling; but it did not seem to be so closely connected with the miscibility of molten metals kept fluid throughout. As regards avoiding loss by oxidation during fusion and volatilisation of zinc, he had found that a little cyanide of potassium previously fused in the melting pot largely if not entirely prevented both sources of alteration; and was preferable for this purpose to borax or metaphosphate of soda, &c., as these substances did not exert any reducing action, but simply cleansed the metal by dissolving any oxide that might be formed.

94. "The Constitution of the so-called mixed Azo-compounds." By Francis R. Japp, F.R.S., and Felix Klingemann, Ph.D.

The authors find that diazobenzene chloride interacts with ethylic sodiomethacetoacetate to form acetic acid and an ethereal salt, $C_{11}H_{14}N_2O_2$ (m. p. 117°), which by hydrolysis is converted into the acid $C_9H_{10}N_2O_2$ (m. p. 185°). They have also prepared homologues of these compounds, substituting ortho- and para-diazotoluene for diazobenzene, and ethylic ethacetoacetate for methacetoacetate. They at first regarded the acid $C_9H_{10}N_2O_2$ as benzene-azo-propionic acid, $C_6H_5{\cdot}N_2{\cdot}CH(CH_3){\cdot}COOH$ (see *Ber.*, 20, 2942). It yields on reduction a hydrazo-acid, $C_9H_{12}N_2O_2$ (m. p. 170°), which proved to be the α-phenylhydrazidopropionic acid of Fischer and Jourdan, obtained by reduction of phenylhydrazinepyruvic acid. On comparing the supposed benzene-azo-propionic acid with phenylhydrazinepyruvic acid, it was found that the two compounds were identical, the melting point (169°) given by Fischer and Jourdan being much too low. It therefore appeared probable that the acid was a hydrazide: this view is supported by the following proof that "benzene-azo-acetone," hitherto formulated $CH_3{\cdot}CO{\cdot}CH_2{\cdot}N_2{\cdot}C_6H_5$, is in reality a hydrazide of the formula $CH_3{\cdot}CO{\cdot}CH : N{\cdot}NHC_6H_5$, derivable from pyruvic aldehyde.

By acting on "benzene-azo-acetone" with sodium ethoxide and ethylic chloracetate, an ethereal salt was obtained which on hydrolysis yielded an acid of the formula $C_{11}H_{12}N_2O_3$ (m. p. 161—162°). By reduction this acid gave anilido-acetic acid, but no aniline, thus proving that it has the formula $CH_3{\cdot}CO{\cdot}CH : N{\cdot}N(C_6H_5)CH_2{\cdot}COOH$. If "benzene-azo-acetone" had the formula hitherto ascribed to it, the introduction of $CH_2{\cdot}COOH$ into the methylene-group would have occurred and the resulting compound would have yielded aniline on reduction.

The above view is confirmed by the fact that the phenylhydrazide of "benzene-azo-acetone" proves to be identical with the dihydrazide $C_6H_5NH{\cdot}N : CH{\cdot}C(CH_3) : N{\cdot}NHC_6H_5$, recently obtained by von Pechmann from methylglyoxal (pyruvic aldehyde) and phenylhydrazine.

The authors therefore regard the various so-called mixed azo-compounds obtained by the action of diazo-salts upon compounds of the ethylic acetoacetate type as hydrazides. They point to the parallel case of the formation of isonitroso-compounds (hydroximes) by the action of nitrous acid, and suggest that this analogy would be more perfect if *free* diazobenzene were regarded as the anilide of nitrous acid, thus: $ON{\cdot}NHC_6H_5$. Experiments are being undertaken in support of this view. They had intended to study the action of reducing agents on the alkyl-derivatives of the benzene-azo-naphthols

in order to settle the question, already mooted by Zincke, as to whether the latter are azo-compounds or hydrazides; but have renounced this intention on learning that Professor Meldola is engaged in investigating this subject.

95. "The Interpretation of Absorption-Spectra." By G. H. Bailey.

96. "The Reduction of Potassium Bichromate by Oxalic Acid." By C. H. Bothamley, Assistant Lecturer on Chemistry, Yorkshire College.

Potassium bichromate and hydrated oxalic acid, finely powdered and intimately mixed, interact spontaneously after two or three hours, or instantly if heated to 30—35°; after heating at 110—120° until the weight is constant, a dark friable residue is obtained which is completely soluble in water. If the mixture which has been heated at 110—120° is heated over a low flame, care being taken to avoid fusion, further decomposition ensues, and on treatment with water chromic oxide remains undissolved and a solution of potassium chromate free from oxalic acid and chromic salts is left.

If dehydrated oxalic acid be taken the interaction does not take place spontaneously, but occurs instantly at 30—35°, the product being a very bulky porous and friable grey solid; the nature and limit of the interaction is, however, the same as with the hydrated acid.

With an excess of oxalic acid, reduction is complete, but with excess of bichromate the interaction is different. The first stage of the interaction, which takes place at a temperature not exceeding 120°, is represented by the equation $2K_2Cr_2O_7 + 6H_2C_2O_4 = Cr_2(C_2O_4)_3 + 6H_2O + 6CO_2 + 2K_2CrO_4$. The decomposition is limited, even in presence of excess of bichromate, by the formation of chromic oxalate, which is not further oxidised at 120°. At a higher temperature in presence of only a slight excess of bichromate the chromic oxalate decomposes in accordance with the equation $Cr_2(C_2O_4)_3 = Cr_2O_3 + 3CO + 3CO_2$. If, however, a considerable excess of bichromate is present further oxidation takes place thus: $2K_2Cr_2O_7 + Cr_2(C_2O_4)_3 = 2Cr_2O_3 + 6CO_2 + 2K_2CrO_4$. The complete oxidation of oxalic acid in presence of a large excess of potassium bichromate is represented by the equation $4K_2Cr_2O_7 + 6H_2C_2O_4 = 2Cr_2O_3 + 4K_2CrO_4 + 6H_2O + 12CO_2$.

97. "The Reduction of Chlorates by the Zinc-copper Couple." By C. H. Bothamley and G. R. Thompson.

When a solution of potassium chlorate is reduced by means of the zinc-copper couple (Thorpe, Trans., 1873, 541) a portion of the reduced chloride is converted into zinc oxychloride, which is

insoluble in water but readily soluble in dilute sulphuric acid. The quantity of oxychloride formed is greater the more concentrated the solution. In order to avoid the error due to this cause, the chlorate solution is heated with the couple for about one hour, and pure dilute sulphuric acid is then added until the zinc hydroxide and oxychloride just dissolve. The liquid is filtered, neutralised with calcium carbonate and titrated with silver nitrate. Thus modified, the method gives very accurate results; the solution should not contain more than 1·5 gram of potassium chlorate in 25 c.c., and should just cover the couple.

98. "Preliminary Notice on the Oxidation of Oxalic Acid by Potassium Dichromate." By Emil A. Werner, Assistant in the Chemical Laboratory, University of Dublin.

In the course of an investigation of chromoxalates and analogous chromium compounds with other organic acids, the results of which have already been partly published (Trans., 1887, 383), I was led to study the action of oxalic acid on potassium dichromate solutions in presence of sulphuric acid. The results already obtained seem noteworthy, and in view of the fact that a paper on the same or a similar subject is announced, I send the following short note.

In the preparation of the blue chromoxalates already described, 9 mols. of oxalic acid are required for the complete reduction of each molecule of potassium dichromate; in this interaction the oxalic acid is divisible into two distinct portions, viz., 3 mols. which are used up in the reduction of the dichromate, and 6 mols. which combine with the reduced chromium to produce the chromoxalate: *e.g.*, $2KCr_2O_7 + 6H_2C_2O_4 + 3H_2C_2O_4 = K_2H_3Cr_2(C_2O_4)_6 + 7H_2O + 6CO_2$. I have endeavoured to use instead of the persistent 6 mols. oxalic acid their equivalent of succinic acid, but I find that the interaction proceeded in an entirely different manner; only a *partial reduction* of the dichromate is effected by the 3 *mols.* of oxalic acid, and no compound whatever of chromium and succinic acid is produced, the final products of the reaction being:—(1) The red chromoxalate of Crofts, $K_2Cr_2(C_2O_4)_4$, and (2) free $K_2Cr_2O_7$ (about two-fifths of the original amount), the succinic acid remaining unaltered.

If oxalic acid be added until the dichromate is all reduced, 9 *mols. are required*, and the interaction proceeds exactly as in the absence of the succinic acid. An attempt to effect a partial replacement of the oxalic by succinic acid was attended with the same result.

From these results, I was led to investigate more closely the oxidation of potassium dichromate by oxalic acid in presence of sulphuric acid, and while looking over the literature of the subject,

I was struck by the following account of the method of preparing chrome-alum in *Watts' Dictionary* (3rd Supplement). In the preparation of chrome-alum by the action of sulphuric acid on potassium dichromate, the reduction of the latter may be conveniently effected by oxalic acid, when it is not necessary to add an excess of the reagent, as the reaction is complete when CO_2 ceases to be evolved, &c.; the equation representing the change is as follows:—$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2C_2O_4 = K_2Cr_2(SO_4)_4 + 6CO_2 + 7H_2O$. 29·5 parts of dichromate are dissolved in 39 parts of sulphuric acid, and the necessary amount of water, and 38 parts of oxalic acid added gradually in small portions (Lielegg, *Dingl. polyt. J.*, **207**, 321). The production of chrome-alum by this method is entirely dependent on the "necessary amount of water," the above equation being only true when little or no water is present, dilution of the mixture causing only partial reduction of the dichromate, with production of varying amounts of red chromoxalate and chromium sulphate, the former increasing, and the latter diminishing, with the degree of dilution, and *vice versâ*. I am at present engaged in investigating this reaction in all its details, with special reference to the influence of mass and temperature.

The remarkable affinity existing between chromium and oxalic acid as shown in these reactions, becomes all the more interesting when compared with the not less remarkable inert behaviour of chromium towards succinic acid. All attempts hitherto to obtain compounds corresponding to the chromoxalate containing succinic acid have been unsuccessful; in fact *freshly* precipitated chromic hydroxide is perfectly insoluble in excess of succinic acid solution at the boiling temperature, and when heated in sealed tubes at 120—130° C., only a mere trace of the chromium enters into solution.

99. "Isomeric Change in the Naphthalene Series." No. 1. By Henry E. Armstrong.

It having been ascertained that betanaphthylsulphate, $C_{10}H_7{\cdot}OSO_3H$, may be converted by mere warming in the water-bath into the isomeric betanaphtholsulphonic acid (Schaefer's modification), the study of the conditions under which isomeric change occurs in the case of naphthalene-derivatives became of special importance in determining the laws which govern substitution in the naphthalene series, and indeed generally. Experiment soon showed that there were important differences to be observed: thus bromobetanaphthol gave but little sulphate, being almost entirely—and *apparently* directly—converted nto the isomeric acid which may be prepared by brominating Schaefer's betanaphtholsulphonic acid; in like manner, betanaphthyl-

sulphate when sulphonated by chlorosulphonic acid does not yield, as might have been expected, a sulphosulphate but an isomeric disulphonic acid. This latter acid is of special interest on account of the readiness with which, by mere warming with dilute sulphuric acid, it is converted into Schaefer's betanaphtholmonosulphonic acid: there is little doubt that one of the sulphonic groups occupies an alpha-position contiguous to the OH, and hence the readiness with which it is displaced by hydrogen. These observations have not only led to the experiments being made of which the results are described in the following notes, but they have served in connexion with the observations on the sulphonation of naphthalene to favour the assumption that the action of sulphuric acid is in the majority of cases of a very simple character, and that when isomers are produced their formation is very frequently the outcome of isomeric change. The author proposes to pay special attention to the investigation of this question, and not only in the naphthalene series.

100. "Isomeric Change in the Naphthalene Series. No. 2. β-Ethoxynaphthalenesulphonic Acids." By E. G. Amphlett and Henry E. Armstrong.

In order to determine the course of chemical change when the formation of the sulphate is prevented, the authors have sulphonated by means of chlorosulphonic acid the ethoxynaphthalene, $C_{10}H_7{\cdot}OC_2H_5$, prepared by ethylating betanaphthol. The product obtained when a cold solution in carbon bisulphide is operated upon is a mixture of two sulphonic acids, one of which is undoubtedly derived from Schaefer's modification of betanaphtholsulphonic acid, and the other probably from Baeyer's modification; if the product be heated in the water-bath, the latter acid is converted by isomeric change into the former.

The two acids are readily distinguished by means of their barium salts: that of the former acid being almost insoluble in water, while that of the latter dissolves easily and crystallises in transparent prisms containing $3H_2O$. On submitting the difficultly soluble potassium salt from the former acid to the action of bromine, a difficultly soluble ethoxybromosulphonate is obtained; and on further treatment with bromine the bromhydroxyquinonesulphonate is produced which may be prepared in a similar manner from Schaefer's acid. Altogether different results are obtained on heating the isomeric ethoxy-acid with bromine. Experiments are in progress with other derivatives of both α- and β-naphthol in which the hydroxylic hydrogen is displaced by positive and negative radicles.

101. "Isomeric Change in the Naphthalene Series. No. 3. β-Chloronaphthalenesulphonic Acids." By Henry E. Armstrong and W. P. Wynne.

The authors have previously shown that when β-chloronaphthalene is sulphonated by means of chlorosulphonic acid, the product consists of the two isomeric monosulphonic acids which Arnell obtained by using fuming sulphuric acid: one of these is the $\beta^2\beta^{3'}$-derivative corresponding to Schaefer's betanaphtholsulphonic acid, and it was of importance to determine whether this acid was a primary product of sulphonation or a product of isomeric change. It is found that a small proportion—very few per cent.—of the $\beta^2\beta^{3'}$ acid is formed even when the sulphonation is effected by adding the chlorosulphonic acid to a cold solution of β-chloronaphthalene in carbon bisulphide, and that heating on a water-bath has little or no effect; but that if the product be heated to a temperature at which it is just fused—about 150°—for an hour, an appreciably larger proportion of the $\beta^2\beta^{3'}$ acid is obtained, and that after heating for five hours at 150° the product chiefly consists of this acid. There can be little doubt therefore that the $\beta^2\beta^{3'}$ acid is a product of isomeric change.

102. "Isomeric Change in the Naphthalene Series. No. 4. α-Haloidnaphthalenesulphonic Acids." By Henry E. Armstrong and S. Williamson.

The authors have previously shown that when α-chloro-, or α-bromonaphthalene is sulphonated by means of chlorosulphonic acid the product mainly consists of the 1:4-derivative together with a very small proportion of what is probably the 1:2-derivative. They now find that if the product be heated at 150°, isomeric change takes place, new acids being formed of which the constitution has yet to be determined.

It has been stated by Gessner that when potassium α-bromonaphthalenesulphonate in heated with PCl_5 it is converted into a chloronaphthalenesulphobromide melting at 115°. The authors have obtained the normal product, bromonaphthalenesulphochloride, which melts at 101°; but on heating potassium chloronaphthalenesulphonate with PBr_5, they obtained a substance precisely like that described by Gessner and which gave similar results on analysis: this, however, they find is a mixture or compound of chloronaphthalenesulphobromide and bromonaphthalenesulphochloride, and they are inclined to attribute its formation to the presence of free bromine in the PBr_5, and that of Gessner's product to free chlorine in the PCl_5 used by him.

Jolin's statements regarding the properties of bromonaphthalene-

sulphonic acid, which do not accord with their own, are no longer surprising now that the occurrence of isomeric change on heating is established; the authors have moreover observed that when bromonaphthalene is heated with excess of sulphuric acid the bromine is displaced, a naphthalenedisulphonic acid being formed; it is not improbable that the dibromonaphthalene melting at about 160° which Jolin obtained was formed from a naphthalenedisulphonic acid.

103. "The Sulphonation of Naphthalene." By Henry E. Armstrong and W. P. Wynne.

After a very careful study of the products of the direct sulphonation of naphthalene and of the naphthalenemonosulphonic acids by means of chlorosulphonic acid, the authors are convinced that the initial action is always of a simple character and takes place in accordance with what one of them has termed the alpha-law; and as they have also failed to obtain any evidence of the occurrence of isomeric change in the case of the sulphonic acids, they are of opinion that the formation of β-sulphonic acids is due to secondary change, and probably involves the formation and subsequent partial hydrolysis of a higher sulphonic acid than that which is eventually separated. Thus they find that naphthalene may be almost entirely converted into the α-monosulphonic acid by careful treatment with a single molecular proportion of chlorosulphonic acid, and that the sole product of the action of 2 mol. props. is the $\alpha'\alpha''$ or γ-disulphonic acid; the pure β-monosulphonic acid in like manner yields as sole product the β (?)-disulphonic acid previously described by them, which is undoubtedly an α-β-derivative—in all probability the 2 : 4′ modification. By heating naphthalene with a considerable excess of chlorosulphonic acid at about 150°, they have obtained a trisulphonic acid. This acid yields a very soluble lead salt. Its sodium salt crystallises in aggregates of very slender needles of the composition $C_{10}H_5(SO_3Na)_3{\cdot}5H_2O$; its sulpho-chloride melts at 194°. Experiments are in progress to determine the nature of the trisulphonic acids formed in a similar manner from the β (?) and Ebert and Merz's two disulphonic acids.

To determine whether the sulphonic acids undergo isomeric change, an aqueous solution of the β (?)-disulphonic acid was heated in an air current at a temperature gradually rising to 170—180°, at which it was maintained for several hours: much naphthalene sublimed, and the residue was found to consist almost entirely of the β-monosulphonic acid. Ebert's and Merz's α-disulphonic acid treated similarly underwent no change. On evaporating the water from a solution of α-monosulphonic acid as far as possible at 100° and then raising the temperature to 115°, hydrolysis immediately sets in.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Olfactics and the Physical Senses, by C. H. Piesse. London 1887. From the Author.

A Short Manual of Analytical Chemistry. Qualitative and Quantitative—Inorganic and Organic, by J. Muter, 3rd edition. London 1887. From the Author.

Experimental Chemistry for Junior Students. Part IV. Chemistry of the Carbon Compounds or Organic Chemistry, by J. E. Reynolds. London 1887. From the Author.

A Course of Quantitative Analysis for Students, by W. N. Hartley. London 1887. From the Publishers.

The Elements of Chemistry, a Text-book for Beginners, by I. Remsen. London and New York 1887. From the Publishers.

Steven Hoogendijk de Stichter van het eerste Stoomwerktuig in Nederland, door A. Huet. Rotterdam 1887.

From the Bataafsch Genootschap.

II. *By Purchase.*

Chimie organique. Essai analytique sur la déterminations des fonctions, par P. Chastaing and E. Barillot. Paris 1887.

Grundriss der Edelsteinkunde, von P. Groth. Leipzig 1887.

Die Beziehungen zwischen dem Siedepunkte und der Zusammensetzung chemischer Verbindungen, von W. Marckwald. Berlin 1887.

Das Princip der Erhalting der Energie, von M. Planck. Leipzig 1887.

Die galvanische Kette mathematisch bearbeitet, von G. S. Ohm. Neudruck mit einem Vorwort, von J. Moser. Leipzig und Wien, 1887.

Die Presskohlen-Industrie, von E. Preissig. Freiberg 1887

Lehrbuch der physiologischen und pathologischen Chemie, von G. Bunge. Leipzig 1887.

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ABSTRACTS OF THE PROCEEDINGS

OF

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DATES OF ISSUE OF THE MONTHLY NUMBERS OF THE JOURNAL OF THE CHEMICAL SOCIETY TO FELLOWS.

January number	was issued	7th January.
February	,,	3rd February.
March	,,	9th March.
April	,,	6th April.
May	,,	5th May.
June	,,	7th June.
July	,,	6th July.
August	,,	2nd August.
September	,,	1st September.
October	,,	3rd October.
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December	,,	5th December.
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Bannar, Samuel	December 15th, 1887.	February 2nd.
Barbour, Thomas Fraser	January 19th	February 16th.
Barraclough, William Herbert	„ „	„ „
Belcher, John Hope	November 1st	December 6th.
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Lawson, Thomas A.	December 1st, 1887.	February 2nd.
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Mayhew, Edward W. A. A.	May 3rd	June 7th.
Mayne, James	January 19th	February 16th.
Miers, Henry Alexander	May 17th	June 21st.
Mousley, Frank	,, ,,	,, ,,
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Munroe, Charles E.	February 2nd	March 15th.
Overbeck, Otto	January 19th	February 16th.
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Parsons, William	April 5th	May 17th.
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Ramsay, A. Alexander	June 21st	November 15th.
Reynolds, Henry Charles	April 5th	May 17th.
Rhodes, Clement T.	June 7th	November 15th.
Richardson, Clifford	January 19th	February 16th.
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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 46. Session 1887–88.

January 19th, 1888. Mr. William Crookes, F.R.S., President, in the Chair.

Mr. J. Garnett Heywood was formally admitted a Fellow of the Society.

The President announced that the Council nominated as Foreign Members Professors Genther, Ladenburg, Landolt, Nilson, Van't Hoff, Wislicenus and Mons. Lecoq de Boisbaudran; and that these would be balloted for at the next meeting.

Certificates were read for the first time in favour of Messrs. William Herbert Barraclough, Westfield House, Thorpe Hesley, near Rotherham; Thomas Fraser Barbour, 16, Gladstone Terrace, Edinburgh; Henry Dudley Berridge, 203, Bellevue Road, Leeds; Alfred Edward Carey, M.Inst.C.E., 9, Dean's Yard, Westminster; Lewis Smith Cocking, Martin Bank, Huddersfield; Walter Hepworth Collins, 14, Bradford Chambers, Mawdsley Street, Bolton-le-Moors, Lancashire; Astley Cooper, 66, Queen's Road, Headingly; John H. J. Dagger, 3, West Bank Road, Edge Lane, Liverpool; Benjamin Henry Gerrans, Jun., 47, Aubert Park, Highbury, N.; Christopher James, Ida Villa, Swansea; J. Lewkowitsch, 6, Warwick Place, Leeds; Charles Robert Lafosse, Knolls House, Hr. Broughton, Manchester; Frederick K. S. Lowndes, 4, Plumstead Common Road, Woolwich; Thomas Maben, 2, Eskdaill Terrace, Hawick; James Mayne, 203, Oxford Street, Sydney, New South Wales; Otto Overbeck, Wootton Bassett, Wilts; Clifford Richardson, Office of the Engineer Commissioner, Washington, U.S.A.; Robert Mason Sumner, 50, Lord Street, Liverpool; Sam. Smith, 30, Commercial Street, Batley, Yorkshire; Angus Smith, 5, Antigua Street, Greenock; Arthur J. C. Waterland, Sidney Villa, South West Road, Leytonstone;

John Cuthbert Welch; Emil A. Werner, 5, Church Avenue, Rathmines, Dublin.

The following papers were read:—

1. "Morindon." By T. E. Thorpe, F.R.S., and W. J. Smith, M.B.

The authors have confirmed the observations of Thorpe and Greenall (*Chem. Soc. Trans.*, 1887, 52) on Morindon. Morindin, the active colouring matter of Al, the root-bark of *Morinda citrifolia*, yields 48·4 per cent. of moridon on hydrolysis. This latter substance is not identical with alizarin, but has the composition $C_{15}H_{10}O_5$, and differs from all of the eight compounds of the same formula which are known at present.

That morindon is a methylanthracene-derivative has been proved by distilling it with zinc-dust. The methylanthracene so obtained was oxidised by chromic acid to anthraquinonecarboxylic acid having all the properties described by Liebermann.

2. "Manganese trioxide." By T. E. Thorpe, F.R.S., and F. J. Hambly.

The authors have repeated the experiments of Franke (*Journ. für Prakt. Chemie*, 1887) on the so-called volatile oxides of manganese. They have been unable to obtain any evidence of the existence of the blue gaseous manganese tetroxide. They find, however, that *manganese trioxide* exists and can be formed by the action of a solution of potassium permanganate in sulphuric acid on dry sodium carbonate. It is a reddish-pink amorphous solid, extremely deliquescent, and stable only at a low temperature. On heating it is at once decomposed into manganese dioxide and oxygen. Water decomposes it into manganese dioxide and permanganic acid.

3. "Note on Chatard's process for the estimation of small quantities of manganese." By the same.

The authors find that the inconvenience arising from the formation of lead carbonate in the titration of permanganic acid by ammonium oxalate may be obviated by adding sulphuric acid when boiling with the lead dioxide and nitric acid without impairing the accuracy of the results.

Discussion.

In reply to a question by the President, Mr. Hehner said that Chatard's method was an extremely delicate one; using it in the form

of a colorimetric process. he had been able to detect manganese in a few mgrms. of steel containing only half a per cent. of manganese.

Professor Thorpe, also in reply to the President, said that there was no reason to believe that any volatile oxide of manganese existed. Chatard's was essentially a minimetric method, and gave highly satisfactory results with very small quantities of manganese.

4. "Contributions to the theory of the vitriol-chamber process." By G. Lunge.

The theory has been recently advanced by Raschig that the vitriol-chamber process involves the formation in the first instance from nitrous acid and sulphurous acid of dihydroxylaminesulphonic acid, which being acted on by nitrous acid yields sulphuric acid and nitric oxide; this nitric oxide he considers is then reconverted into nitrous acid. This theory is regarded by the author as untenable on all points. It completely ignores the existence of nitrosyl sulphate (chamber-crystals); moreover, according to Raschig's own investigation, the dihydroxylaminesulphonic acid, as it could not possibly meet at all points with nitrous acid, would yield N_2O, of which a very large quantity would be found in the chambers, which is never the case; lastly, nitric oxide, oxygen in excess and water do not yield nitrous acid but nitric acid. Raschig's indirect proofs are equally unsatisfactory, and would at most only show that subsidiary reactions may take place to a small extent.

A true theory of the vitriol-chamber process must deal with the substances actually present and with reactions fully proved to take place. It has been already foreshadowed by the author (*Chem. Soc. Trans.*, 1885. 470) in these words: "It is not as hitherto generally assumed NO, but N_2O_3, which acts as carrier of the oxygen in the vitriol chamber, &c." The principal reactions are:—

$$2SO_2 + N_2O_3 + O_2 + H_2O = 2SO_2(OH)(ONO).$$
$$2SO_2(OH)(ONO) + H_2O = 2SO_2(OH)_2 + N_2O_3.$$

These reactions are modified in the first part of the chambers by the excess of SO_2; in the last part sometimes by the complete absence of SO_2; and in some places by an excess of water. No theory can be accepted which assumes the formation of NO_2, since this gas does not occur at all in normally working chambers, and since its formation is practically excluded by the conditions which obtain in the end chambers. The question whether N_2O_3 exists as a gas or not plays only a secondary part in this discussion; but the phenomena occurring in the vitriol-chambers make it at least more probable that N_2O_3 must exist as a gas for some time before it is dissociated. At all events the

gas present in the back chambers has a composition equivalent to N_2O_3, and this or NO(OH) must be introduced into the reactions. The direct reactions: $SO_2 + N_2O_3 + H_2O = SO_2(OH)_2 + 2NO$, and $4NO + O_2 = 2N_2O_3$, cannot any longer be considered as important, since nitric oxide and oxygen do not yield N_2O_3 except in immediate contact with sulphuric acid—when $SO_2(OH)(ONO)$ is formed; apart from this, NO_2 must be formed in dry places, or NO_3H in the presence of water, but the presence of SO_2 modifies everything.

In the front chambers there is much NO present along with N_2O_3. NO is formed by a secondary reaction (denitration) from nitrosyl sulphate: $2SO_2(OH)(ONO) + SO_2 + 2H_2O = 3SO_4H_2 + 2NO$, and is principally absorbed by the direct reaction—$4SO_2 + 4NO + 3O_2 + 2H_2O = 4SO_2(OH)(ONO)$; none of it can pass into NO_2, but some of it may pass into NO_3H, which is at once acted upon by SO_2, and converted into nitrosyl sulphate. Thus the normal vitriol-chamber process is not as hitherto understood an alternation of reductions and oxidations, but it is a *condensation* of nitrous acid, or of NO with SO_2 and O_2 to nitrosyl sulphate, and a splitting up of the latter into sulphuric acid and N_2O_3.

Abnormally, N_2O can be formed by the reduction of NO by SO_2, but not according to Raschig's theory. This reaction in properly working chambers does not exceed an extent of 0·5 part of $NaNO_3$ on 100 of S.

Much larger losses are sometimes caused by the abnormal formation of NO_2 in the back chambers, which is due to an abnormally great supply of nitre. In this case the acid-forming process is finished too soon: the N_2O_3 does not meet with any more SO_2, and thus finds time to dissociate into NO and NO_2. Another abnormality is caused by a deficiency of nitre, which leads to losses in the shape of N_2O, of NO, and of NO_3H. Much importance is due to the fact that the normal working of the acid-forming process is a mass reaction, requiring a great excess of oxygen, without which the denitrating reactions, normally prevailing in the front chamber, set in abnormally in the back chamber. This leads to an explanation of the fact why larger chamber-space and a more copious supply of nitre compensate each other to a certain extent.

Discussion.

Dr. Alder Wright thought that an argument might perhaps be adduced in favour of the predominance of NO in the earlier chambers of a series as compared with N_2O_3, from the colour of the gases, the pale colour of which (as contrasted with the tint that would be seen were all nitrous fumes present as N_2O_3) would suggest that only a

small fraction of the gases was in the higher state of oxidation. He was disposed to believe that in the chambers themselves *sulphur dioxide* was capable of reducing higher oxides of nitrogen not only to NO but even to N_2O and N_2. This was generally considered to be brought about in the Glover tower in virtue of the higher temperature, and also of the presence of As_2O_3 from pyrites; but as nitrous fumes were known to be destroyed (presumably by reduction) when no Glover tower was used, and with brimstone acid where little or no arsenic was present, it appeared to him that some other source of such loss must be looked for, and that this was to be found in the power of sulphur dioxide to reduce oxides of nitrogen to nitrous oxide at a lower temperature than usually supposed possible.

Professor Ramsay said that Dr. Lunge's remark that nitrous anhydride might act as such, or as a mixture of nitric oxide and peroxide, is, so far as the last statement is concerned, in complete accordance with Professor Ramsay's experience. A mixture of NO_2 and NO in the proportion necessary to form N_2O_3 will act as such with such reagents as water or sulphuric acid. With regard to Dr. Wright's remarks on the production of nitrous oxide, Professor Ramsay had heard from alkali makers that when "things went wrong," *i.e.*, when excess of sulphur dioxide was present, such reduction does take place.

NOTICE TO AUTHORS OF PAPERS.

To facilitate the preparation of the abstract accounts of the Proceedings at the meetings of the Society, all authors are requested to furnish abstracts of their communications, and to send their papers so that they may be in the hands of the Secretaries, if possible, on the Monday before the day of meeting. Authors are also requested to write on their papers *the address to which they wish proofs to be sent.*

At the next meeting, on February 2nd, a lecture will be delivered on "The Range of Molecular Forces," by Professor Rücker, M.A., F.R.S.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 47. Session 1887–88.

February 2nd, 1888. Mr. William Crookes, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. Thomas Ashcroft Ellwood, 46, St. Mary's Terrace, Paddington; James H. Gardiner, 6, Bloemfontine Avenue, Uxbridge Road, W.; Charles E. Munroe, Newport, Rhode Island, U.S.A.; Herbert Trewby, Langford Lodge, Clapham Park, S.W.; Thomas Edward Towerson, care of Messrs. R. Hammond and Co., Bilbao, Spain.

Professors Geuther, Ladenburg, Landolt, Nilson, Van't Hoff, Wislicenus and M. Lecoq de Boisbaudran were elected Foreign Members of the Society.

The following were elected Fellows of the Society:—Messrs. Edward Arthur Andrews, Samuel Banner, Arthur G. Bloxam, Peter Coulson Bunn, F. Barker Cooke, Albert W. Day, Philip A. Estcourt, William Cay Forsyth, Agnew Griffith, Lewis Walter Hawkins, John B. Kirkland, Thomas A. Lawson, Ph.D., Frank E. Lease, Stevenson J. C. G. Macadam, Edmund G. McBretney, W. Sedgwick Saunders, Frederick W. Shaw, Sidney Skinner, B.A., Charles F. Townsend, Alfred Edwin Tutton.

The following lecture was delivered:—

5. "The Range of Molecular Forces." By A. W. Rücker, M.A., F.R.S.

In discussing the range of molecular forces it is convenient to adhere to the language of the theory of action at a distance, though with full expectation that it will ultimately be replaced by another,

such as the vortex-atom theory of Sir W. Thomson, or the granular theory of Professor Osborne Reynolds, which involves only action in proximity.

If we do this, however, it must be admitted that the law of molecular action may be very complicated. It may be granted that we naturally look for simplicity in our fundamental assumptions, but it is certain that we have *à priori* no more right to expect simplicity in the results of the action of a medium than simplicity in its constitution, and that the two are not necessarily obtained together.

The largest values of the magnitude of the radius of molecular action which have been published have been deduced from observations on the condensation of gases and vapours on the surfaces of solids. Estimates on this basis made by Müller-Erzbach (*Exner's Rep.*, 1885, **21**, 409) and Kayser (*Wied. Ann.*, 1881, **14**, 450) have ranged between 1500 and 3000 micromillimetres* ($\mu.\mu$). Such observations are open to many objections. Bunsen (*Wied.*, 1885, **24**, 335) has shown that CO_2 will not condense on glass unless a film of water be previously formed. Warburg and Ihmori (*Wied.*, 1886, **27**, 481, and *Wied.*, 1887, **31**, 1006) adduce reasons for believing that the water film is largely due to uncombined or loosely combined alkalis on the surface. On clean unvarnished metals, washed glass and quartz, the thickness of the water film which can be removed by dry air without heating does not exceed 12 $\mu.\mu$. A striking exception is agate, on which films 1640 $\mu.\mu$. thick are stated to have been formed. As this substance, however, is composed of alternate layers of quartz and a porous impure opal the basis for an accurate calculation does not exist.

On the whole, it seems that no definite conclusions as to the magnitude of the radius of molecular action (ρ) can at present be drawn from these experiments.

Quincke (*Pogg. Ann.*, 1869, **137**, 402), as is well known, by measuring the capillary elevation of liquids between glass plates coated with thin wedged-shaped films, found $\rho = 50\ \mu.\mu$.

Plateau (*Statique des Liquides*, 1873, **1**, 210) showed that the surface-tension of a soap-bubble, which thinned until its thickness was 118 $\mu.\mu$., was unaltered. He concluded that $\rho < 59\ \mu.\mu$. Maxwell (*Ency. Brit.*, Ed. ix, Art. "Capillary Action"), however, though by a confessedly imperfect theory, shows that the surface-tension may not change until the thickness of the film $= \rho$. Hence Plateau's result may mean only that $\rho < 118\ \mu.\mu$.

Reinold and Rücker (*Phil. Trans.*, **177**, Part ii, 1886, 627) have proved that the surface-tension does not alter by 0·5 per cent., when the film is so thin as to show the black of the first order of Newton's

* The micromillimetre is the millionth of a millimetre.

colours. This appears at first sight at variance with Quincke's result, but their observations are really in remarkable accord with his.

The black and coloured parts of a film are separated by a sharp line, which proves a discontinuity in the thickness (*Proc. Roy. Soc.*, 1887, No. 182, 340). The colours, which correspond to certain thicknesses, which may be called the unstable range of thickness, are always missing.

The black part of the film has been proved by Reinold and Rücker (*Phil. Trans.*, Part II, 1883, 645) to be of a uniform thickness, which differs but little from 12 $\mu.\mu.$ Sir William Thomson (*Proc. Royal Institution*) and these observers independently arrived at the conclusion that these curious phenomena are due to the fact that the surface-tension diminishes to a minimum, and then increases again when the thickness is somewhat >12 $\mu.\mu.$

The colours of the film prove that the upper limit of the range of unstable thickness is between 96 and 45 $\mu.\mu.$ Quincke's result indicates that it lies between 100 $\mu.\mu.$ and 50 $\mu.\mu.$, according as we adopt Plateau's or Maxwell's views. These calculations are therefore in complete accord. Quincke's result is not an isolated fact, but is supported by observations on soap films. The statement that 50 $\mu.\mu.$ and the radius of molecular action are of the same order of magnitude may now perhaps rank as an ascertained fact.

Another method of investigating the radius of molecular action is based on the phenomena of electrolytic polarisation, by observing the change in the difference of potential between a metal and a liquid in which it is immersed, when a gas or metal is deposited on it by electrolysis. In the former case we do not know the density of the gas, in the latter Oberbeck (*Wied.*, 1887, **31**, 337) concludes that a plate of platinum is completely polarised by a film of another metal of from 3 to 1 $\mu.\mu.$ in thickness. The method of experiment is, however, open to objections which are indicated by Oberbeck himself.

Measurements of the thickness of the double electric layer of Helmholtz, which is closely related to the distance between two consecutive layers of molecules, have been made by Lippmann (*Compt. rend.*, 1882, **95**, 687), and Oberbeck and Falck (*Wied.*, 1884, **21**, 157). The values they give vary between 1 and 0·02 $\mu.\mu.$ Wiener (*Wied.*, 1887, **31**, 624) has studied the alteration in the phase of light reflected from very thin silver plates deposited on mica. He finds that the effect begins to alter when the thickness is reduced to 12 $\mu.\mu.$, and that it was possible to detect a silver film the thickness of which did not exceed 0·2 $\mu.\mu.$

The diameter of a molecule is a conventional term for the mean distance of the centres of two molecules during an encounter. It may therefore be different in the liquid and gaseous states. Sir William Thomson (*Natural Philosophy*, Thomson and Tait, Part II, 295, 1883),

as the result of his celebrated discussion of this point, concludes that the mean distances between the centres of molecules in liquids (supposed arranged uniformly) is between 0·07 and 0·02 $\mu.\mu.$, and that the latter quantity is an inferior limit to the diameter of a gaseous molecule.

The diameters of molecules (d) may be calculated if we know the mean free path (L), and the so-called condensation coefficient (v), which is the volume of the molecules contained in a unit volume of the gas.

Loschmidt (*Sitzungsber. Wien. Akad. Math. Classe*, **52**, abt. 2), and O. Meyer (*Die Kinetische Theorie der Gase*, 225, 1887) have calculated d on the assumption that the molecules in a liquid practically fill the whole space it occupies. Exner (*Rep. der Physik*, **21**, 226, 1885), using a formula given by Clausius, $v = (K - 1)/(K + 2)$, when K is the specific inductive capacity, and which may be replaced by $v = (n^2 - 1)/(n^2 + 2)$, when n is the refractive index, finds values of d about five times smaller.

Three independent methods of calculating the diameter of a gaseous hydrogen molecule lead to results between 0·14 and 0·11 $\mu.\mu.$ The most reliable conclusions which have been reached as to molecular magnitudes may be summed up in the following table, which is reproduced from a diagram exhibited during the lecture.

$\mu.\mu.$		
118	Superior limit to ρ	Plateau. (Maxwell).
96—45	Range of unstable thickness begins	Reinold and Rücker.
59	Superior limit to ρ	Plateau.
50	Magnitude of ρ	Quincke.
12	Range of unstable thickness ends	Reinold and Rücker.
12	Action of silver plate on phase of reflected light alters	Wiener.
10·5	Thickness of permanent water film on glass at 23° C.	Bunsen.
4—3	Mean distance between centres of molecules in gases at 760 mm. and 0° C.	O. Meyer.
3—1	Thickness of metal films which polarise platinum	Oberbeck.
1—0·02	Thickness of electric double layer	Lippmann and Oberbeck.
0·2	Smallest appreciable thickness of silver film	Wiener.
0·14—0·11	Diameter of gaseous hydrogen molecule	Exner. O. Meyer. Van der Waals.
0·07—0·02	Mean distance between centres of liquid molecules	W. Thomson.
0·02	Inferior limit to diameter of gaseous molecule	W. Thomson.

6. "A New Method of obtaining Monohydrazides of α-Diketones." By Francis R. Japp, F.R.S., and Felix Klingemann, Ph.D.

Nitrous acid interacts with ethylic methacetoacetate, forming ethylic isonitrosopropionate, and with methacetoacetic acid forming isonitroso-ethyl-methyl ketone. The authors recently showed (Proc., 1887, 140) that in the first of these reactions the nitrous acid may be replaced by diazo-salts, in which case an ethylic phenylhydrazine-pyruvate is obtained. They now find that the analogy between nitrous acid and diazo-salts extends also to the second reaction. By acting on sodium methacetoacetate with diazobenzene chloride they have prepared v. Pechmann's monohydrazide diacetyl :—

$$Ac{\cdot}CH(CH_3){\cdot}CO_2Na + C_6H_5{\cdot}N_2Cl = CH_3{\cdot}CO{\cdot}C{\cdot}CH_3 + CO_2 + NaCl$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \ddot{N}{\cdot}NHC_6H_5$$

The compound crystallised in short needles, melting at 133°, which agrees with v. Pechmann's determination. With phenylhydrazine it yields a compound melting at 243°, identical with v. Pechmann's dihydrazide of diacetyl (m. p. 240°; v. Pechmann).

The authors intend to extend this reaction to other alkyl-aceto-acetic acids.

7. "The Formation of Dihydrazides of α-Diketones." By Francis R. Japp, F.R.S., and Felix Klingemann, Ph.D.

The authors find that the compound $C_{16}H_{18}N_4$, which they obtained by heating phenylhydrazinepyruvic (benzene-azopropionic) acid, and which is formed according to the equation $2C_9H_{10}N_2O_2 = C_{16}H_{18}N_4 + 2CO_2 + H_2$ (*Ber.*, **20**, 2943), is identical with the dihydrazide of diacetyl, since prepared by v. Pechmann (see preceding note). Its formation from phenylhydrazine-pyruvic acid may be represented thus—

$$\begin{matrix} CH_3{\cdot}C : (N_2H{\cdot}C_6H_5){\cdot}\overline{COO|H} \\ CH_3{\cdot}C : (N_2H{\cdot}C_6H_5){\cdot}\underline{COO|H} \end{matrix} = \begin{matrix} CH_3{\cdot}C : (N_2H{\cdot}C_6H_5) \\ CH_3{\cdot}C : (N_2H{\cdot}C_6H_5) \end{matrix} + CO_2 + H_2.$$

The authors have prepared the corresponding compounds from the tolylhydrazine-pyruvic acids, and are engaged in comparing them with those obtainable from diacetyl and the tolylhydrazines.

8. "The Action of Phenylhydrazine on an Unsaturated γ-Diketone." By Francis R. Japp, F.R.S., and G. N. Huntly.

The saturated γ-diketones, such as acetonyl-acetone, are known to interact with 2 mol. proportions of phenylhydrazine to form colour-

less dihydrazides: the authors find that an unsaturated γ-diketone—anhydracetophenonebenzil—behaves differently, thus:

$$Ph{\cdot}CO{\cdot}CPh : CH{\cdot}CO{\cdot}Ph + C_6H_5{\cdot}NH{\cdot}NH_2 = C_{28}H_{22}N_2 + H_2O + O,$$

the reduction involved in the process being probably effected at the expense of a second molecule of phenylhydrazine. The compound $C_{28}H_{22}N_2$ forms canary-yellow needles, melting with decomposition at 231°, very sparingly soluble in all the ordinary organic menstrua of low boiling point. The authors regard it as a closed-chain compound, possibly with two nitrogen-atoms in the ring.

9. "The supposed Identity of Rutin and Quercitin." By E. Schunck, Ph.D., F.R.S.

Rutin, a crystalline yellow colouring matter contained in the leaves of garden rue (*Ruta graveolens*), was discovered by Weiss, and subsequently examined by Bornträger; by Rochleder and Hlasiwstz, who obtained it from capers, the flower buds of *Capparis spinosa;* by Stein, who found it in Chinese yellow berries, the flower buds of *Sophora japonica;* and by the author himself, who extracted it from the leaves of *Polygonum fagopyrum*, the common buck-wheat. By most of these chemists it was held to be a distinct substance. The experiments of Hlasiwetz, however, seemed to prove that it was identical with quercitrin, and this view appears to have been generally adopted. Quercitrin having within the last few years been examined by Liebermann and others, and its true composition having been ascertained, while rutin, so far as the author knows, has not recently been made the subject of investigation, it was thought that it might be of interest again to compare the two substances, and, if found to be distinct, to ascertain wherein the difference consists.

The quercitrin employed by the author was obtained from quercitron bark, and was found to have the properties and composition assigned to it by Liebermann and Hamburger. The rutin was derived from buck-wheat leaves, and though it had been in the author's collection for many years had undergone no perceptible change.

A comparative examination of the two substances led to the conclusion that they are indeed extremely similar, but that they differ essentially as regards some of their properties; they also differ in composition.

Rutin yields with acids the same products of decomposition as quercetrin, viz., quercetin and isodulcite, but not in the same relative proportion; it gives less quercetin and more isodulcite. The analyses of rutin agree with the formula $C_{42}H_{50}O_{25}$, that of quercetrin being $C_{36}H_{38}O_{20}$. The process of decomposition with acids would be represented by the equation—

$$C_{42}O_{50}H_{25} + 4H_2O = C_{24}H_{16}O_{11} + 3C_6H_{14}O_6.$$

Hence it would appear that rutin is derived from 1 mol. of quercetin and 3 mols. of isodulcite, and quercitrin from only 2 mols. of the latter and 1 of the former.

10. "The Composition of Bird-lime." By E. Divers, M.D., F.R.S., and M. Kawakita, M.E., F.C.S.

Bird-lime from *Ilex aquifolium* was investigated a few years ago by J. Personne, who found in it, besides vegetable *débris* and water, calcium oxalate, caoutchouc and ethereal salts of a solid, crystalline alcohol, $C_{25}H_{44}O$, m. p. 175°, with undetermined fatty acids. The authors had partly examined Japanese bird-lime before Personne published his results, and were induced to continue their work afterwards by finding that their observations, to some extent, differed from and went beyond his. Indeed, their work renders it probable that Japanese bird-lime, prepared as it is, not from *I. aquifolium*, but from *I. integra*, is different in some respects in composition from European bird-lime.

They find the fatty acids of the ethereal salts to be *palmitic acid*, and, in very small quantity, a semi-solid acid, the calcium salt of which is soluble in ether and in alcohol. They have obtained two very similar alcohols by hydrolysis, one differing only slightly from Personne's *ilicic alcohol*, which they have named *ilicylic alcohol*, and have found from closely concordant analyses to have the composition $C_{22}H_{38}O$; and another, which they have named *mochylic alcohol*, from *mochi*, the Japanese word for (bird-)lime, or glutinous matter, and which agrees closely in composition with the formula $C_{26}H_{46}O$. The melting point of this alcohol is 234° C., and that of ilicylic alcohol, 172°. The two alcohols are separated from each other and from a resinoid body, $C_{26}H_{44}O$, by a tedious process of fractional dissolution with spirit of varying strengths. The resinoid body is readily soluble in spirit as weak as 80 per cent., mochylic alcohol in that of 95 per cent. or stronger, and ilicylic alcohol in that of 85—90 per cent. or stronger. The resinoid body (m. p. 110°) volatilises above 360°, apparently but little changed, ilicylic and mochylic alcohols, without change in a vacuum, at about their respective melting points. Heated with palmitic acid, the two alcohols are converted into compounds just like purified bird-lime. Caoutchouc is also present in Japanese bird-lime to the extent of about 6 per cent.; but only minute quantities of oxalates. By destructive distillation, bird-lime yields much palmitic acid and a thick, oily, hydrocarbon, $C_{26}H_{44}$, besides fluorescent and more carbonaceous hydrocarbons, very little gas, and very little

carbonised residue. The authors consider bird-lime to be closely allied to the *waxes* in chemical constitution.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Études des dissolutions aqueuses, fondée sur les changements de leurs poids spécifiques, par D. Mendeléef. St. Petersburg 1887. (In Russian.) From the Author.

Liquid Fuel. Its advantages for firing Steam Generators, by B. H. Thwaite. Liverpool 1887 (Pamphlet). From the Author.

A Treatise of Chemistry, by H. E. Roscoe and C. Schorlemmer. Vol. III, Organic, Part IV. London 1888. From the Authors.

Notes on the Chemistry of Building Materials for Students of Construction, by A. J. Evans and A. Grenville. London 1887. From the Authors.

Report on Indian Fibres and Fibrous Substances exhibited at the Colonial and Indian Exhibition, 1886, by C. F. Cross, E. J. Bevan, and C. M. King, in association with E. Joynson; with Notes of Methods of Treatment and Uses prevalent in India, by G. Watt. London 1887. From the Authors.

Five-figure Logarithms, by C J. Woodward. London and Birmingham 1887. From the Author.

Arithmetical Chemistry: Parts I and II, by C. J. Woodward, London and Birmingham. From the Author.

The Mineral Resources of the United States for the Year 1886, by D. T. Day, U.S. Geological Survey. Washington 1887. From the Survey.

II. *By Purchase.*

Dix années dans l'histoire d'une théorie. par J. H. Van't Hoff. Rotterdam 1887.

Technical School and College Building, by E. C. Robins. London 1887.

Lectures on the Physiology of Plants, by J. v. Sachs. Translated by H. Marshall Ward. Oxford 1887.

Food Adulteration and its Detection, by J. P. Battershall. New York and London 1887.

A Chapter in the History of Meteorites, by the late W. Flight. London 1887.

Leçons de physiologie expérimentale appliqué à la médecine, par C. Bernard. 2 tomes. Paris 1855.

Leçons sur la physiologie et la pathologie du système nerveux, par C. Bernard. 2 tomes. Paris 1858.

Leçons sur la propriétés physiologiques des liquides de l'organisme, par C. Bernard. 2 tomes. Paris 1859.

Introduction à l'étude de la médecine expérimentale, par C. Bernard. Paris 1865.

Leçons sur les anesthésiques et sur l'asphyxie, par C. Bernard. Paris 1875.

Leçons sur la chaleur animale, sur les effets de la chaleur, et sur la fièvre, par C. Bernard. Paris 1876.

Leçons sur le diabete et la glycogenése animale, par C. Bernard. Paris 1877.

Leçons de physiologie opératoire, par C. Bernard. Paris 1879.

Leçons sur les phénomènes de la vie communs aux animaux et aux végétaux, par C. Bernard. Tome I, 2me ed. Paris 1885; tome II. Paris 1879.

Leçons de pathologie expérimentales et leçons sur les propriétés de la moelle épinère, par C. Bernard. 2me ed. Paris 1880.

Leçons sur les effets des substances toxiques et médicamenteuses, par C. Bernard. Nouveau tirage. Paris 1883.

L'œuvre de Claude Bernard. Introduction, par M. Duval. Paris 1881.

Die stärke umbildende Fermente in den Pflanzen, von J. Baranetzky. Leipzig 1878.

Pharmaceutische Chemie, von F. A. Flückiger, Zweite Auflage. 2 Bände. Berlin, 1888.

Fortschritte der Electrotechnik. Vierteljährige Berichte über die neueren Erscheinungen auf dem Gesammtgebiete der angewandten Electricitätslehre mit Einschluss des electrischen Nachrichten- und Signal-wesen: Unter Mitwirkung von M. Kiliani and E. Pirani, herausgegeben von K. Strecker. Erster Jahrgang: das Jahr 1887; erstes and zweites Heft. Berlin 1888.

NOTICE TO AUTHORS OF PAPERS.

To facilitate the preparation of the abstract accounts of the Proceedings at the meetings of the Society, all authors are requested to furnish abstracts of their communications, and to send their papers so that they may be in the hands of the Secretaries, if possible, on the Monday before the day of meeting. Authors are also requested to write on their papers *the address to which they wish proofs to be sent.*

At the next meeting, on February 16th, there will be a ballot for the election of Fellows, and the following papers will be read:—

"An Analysis of Wackenroder's Solution and an Explanation of the Formation of its proximate Constituents," by Prof. H. Debus, F.R.S.

"Potilitzin's Law of mutual Replacement of Bromine and Chlorine," by Prof. Thorpe, F.R S., and J. W. Rodger.

"The Action of Phosphorus Pentachloride on Salicylaldehyde," by C. M. Stuart.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 48. Session 1887–88.

February 16th, 1888. Mr. William Crookes, F.R.S., President, in the Chair.

Messrs. T. A. Lawson and Edward A. Andrews were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Alfred Chiddey, Mount Costigan Smelting Works, Tuena, New South Wales; Harold Nicolai Faber, 56, Dalberg Road, Brixton; James Hart, 131, Embden Street, Manchester; C. Millard King, 63, Frome Park Road, Hornsey, N.; Vivian Byam Lewes, 18, Park Row, Greenwich, S.E.; Frederick Grevile Ruddock, Wilderspool Road, Warrington; H. Belcher Thornton, 11, Esk Terrace, Whitley, Yorkshire; Edward Arthur Wates, 4, Princes Road, Lewisham, S.E.

It was announced that the following changes in the Council List were proposed by the Council:—

As *Vice-Presidents*, Professors Carey Foster and Mallet, *vice* Professors Dewar and Tilden.

As *Members of Council*, Professors Dunstan, Heaton and Purdie and Dr. Plimpton, *vice* Messrs. Carteighe, Messel, Newlands and Stevenson.

Professors Dunstan and Heaton and Dr. Rideal were appointed by the meeting to audit the Treasurer's accounts.

The following were elected Fellows of the Society:—Messrs. Henry Dudley Bevridge, Thomas Fraser Barbour, William H. Barraclough, Alfred Edward Carey, Lewis Smith Cocking, W. Hepworth-Collins, Astley Cooper, John H. J. Dagger, Benjamin H. Gerrans, Christopher James, Charles R. Lafosse, J. Lewkowitsch, Frederick K. S. Lowindes, Thomas Maben, James Mayne, Otto Werbeck, Clifford Richardson,

Angus Smith, Sam Smith, Robert Mason Sumner, Arthur J. C. Waterland, John Cuthbert Welch, Emil A. Werner.

The following papers were read:—

11. "Chemical investigation of Wackenroder's solution and explanation of the formation of its constituents." By Professor Debus, Ph.D. F.R.S.

"Wackenroder's" solution is the solution formed by the action of sulphuretted hydrogen on an aqueous solution of sulphurous acid till the sulphurous acid is decomposed. The compounds represented by the formulæ $M_2S_3O_6$, $M_2S_4O_6$, $M_2S_5O_6$ and $M_2S_6O_6$, in which M stands for hydrogen or a monovalent metal, are called "Polythionates." The term "acid" is reserved by the author for the so-called anhydrides. The formula SO_2 stands for sulphurous acid, and H_2SO_3 for dihydric sulphite; S_4O_5 for tetrathionic acid, and $H_2S_4O_6$ for hydric or dihydric tetrathionate.

Wackenroder's solution contains, according to our best authors, sulphur in suspension and pentathionic acid in solution. Pure pentathionic acid has never been prepared. The attempts to make salts of the acid also failed. In consequence, Spring a few years ago denied the existence of pentathionic acid, which he declared to be a solution of sulphur in hydric tetrathionate, not in atomic proportions, but of the same description as the solution of sulphur in carbonic sulphide.

To test the correctness of Spring's assertion, the author suggested to Mr. Lewes some experiments with Wackenroder's solution; and Mr. Lewes prepared nearly pure potassic and baric pentathionate. These salts, however, could not be recrystallised from water, but split up in tetrathionates and sulphur: $K_2S_5O_6 = K_2S_4O_6 + S$. Spring, therefore, would not admit that they were pentathionates, but regards them as mixtures of tetrathionates and sulphur.

In order to remove all doubts about the existence or non-existence of pentathionates, and also to explain some reactions of more than ordinary interest which the author had occasion to observe, whilst Mr. Lewes was carrying out his work, he undertook the experimental investigation described in the paper.

The results briefly stated, are as follows: The filtered Wackenroder solution contains—

(*a.*) Sulphur in suspension in very minute drops.

(*b.*) *A new allotropic modification of sulphur in simple solution, and in the colloidal condition.* This new form of sulphur, Sulphur *ĉ*, separates on evaporation of Wackenroder's solution as a yellow, viscous, semi-fluid mass, *partially soluble in much water.* It resembles, in some respects, silica as set free from soluble silicates by strong acids.

(*c.*) Traces of trithionic acid.
(*d.*) Hydric tetrathionate.
(*e.*) Hydric pentathionate.
(*f.*) A polythionate with more sulphur than pentathionates contain, probably hydric hexathionate.

Pure potassic and cupric pentathionates were prepared from Wackenroder's solution, and the reactions of the polythionates carefully investigated. The most interesting of these reactions are *the spontaneous changes of the polythionates in aqueous solutions;* they are indicated by the equations—

(*a.*) $K_2S_5O_6$ = $K_2S_4O_6$ + S
Pot. pentathionate. Pot. tetrathionate.

(*b.*) $2(K_2S_4O_6)$ = $K_2S_3O_6$ + $K_4S_5O_6$.
Pot. tetrathionate. Pot. trithionate. Pot. pentathionate.

(*c.*) $2(K_2S_3O_6)$ = $K_2S_4O_6$ + $K_2SO_4 + SO_2$
Pot. trithionate. Pot. tetrathionate.

(*d.*) $3(K_2S_3O_6)$ = $K_2S_5O_6$ + $2(K_2SO_4 + SO_2)$
Pot. trithionate.

Reactions (*a*) and (*b*) occur reciprocally in either direction with equal facility. From these reactions important conclusions can be drawn with regard to molecular and atomic motion in liquids. The pentathionates resemble persulphide of hydrogen, and are, like ozone and peroxide of hydrogen, endothermic compounds. The similarities which exist, from a chemical point of view, between the polythionates on the one hand and ozone and peroxide of hydrogen on the other, are applied in the paper to explain some of the chief properties of ozone and peroxide of hydrogen.

In the second part of the paper the action of sulphuretted hydrogen and sulphurous acid respectively on the hydrogen salts of the polythionic acids are fully investigated. It is proved that the pentathionic acid of Wackenroder's solution is chiefly derived from the condensation of thiosulphuric acid, thus:—

$5(S_2O_2)$ = $2(S_5O_5)$
Thiosulphuric acid. Pentathionic acid.

$2(S_5O_5) + 2H_2O$ = $2H_2S_5O_6$
Hydric pentathionate.

The final products of the action of sulphuretted hydrogen on hydric tetra- or hydric penta-thionate are water and sulphur. The statement of the text-books that sulphuretted hydrogen and sulphur-

ous acid produce water and sulphur, is, therefore, correct in so far as the final products are concerned. The polythionates are intermediate products.

Sulphurous acid and potassium thiosulphate or sulphurous acid and the chlorides of sulphur, produce salts of the polythionic acids.

The third part of the paper is devoted to the discussion of the formulæ of the polythionates. It is shown that the following formulæ are the most correct expressions of our experience :—

$$\begin{matrix} K\cdot SO_2\cdot O \\ KO\cdot SO_2\cdot \dot{S} \end{matrix}$$
Pot. trithionate.

$$\begin{matrix} KS\cdot SO_2\cdot O \\ KO\cdot SO_2\cdot \dot{S} \end{matrix}$$
Pot. tetrathionate.

$$\begin{matrix} KS_2\cdot SO_2\cdot O \\ KO\cdot SO_2\cdot \dot{S} \end{matrix}$$
Pot. pentathionate.

$$\begin{matrix} KS_3\cdot SO_2\cdot O \\ KO\cdot SO_2\cdot \dot{S} \end{matrix}$$
Pot. hexathionate.

12. "Potilizin's Law of Mutual Displacement of Chlorine and Bromine." By T. E. Thorpe, F.R.S., and J. W. Rodger.

On heating bromine with an equivalent quantity of an anhydrous metallic chloride in a sealed glass tube free from air at the temperature of the melting point of zinc, Potilizin found that the amount of chlorine displaced by bromine was greater the higher the atomic weight of the metal in the chloride. Experiments were made with the chlorides of sodium, potassium, silver, calcium, strontium, barium, lead and mercury. Potilizin further found that if A be the atomic weight of the metal, p the percentage of chlorine displaced from its chloride when treated as above, and E its valency, the formula $\frac{A}{pE^2} = a$ constant, held good in the case of lithium, sodium, potassium, silver, calcium, strontium, barium, lead, mercury, bismuth, tin and iron. He considered the quantity of chlorine displaced to depend on the atomic weight, valency and temperature. Arranging the metals in accordance with the periodic law in vertical series, the chlorine displaced was as the atomic weight, $\frac{A}{p}$ being a constant for each series.

Berthelot pointed out that displacement of chlorine by bromine was only possible if the heat of formation of BrCl was greater than the heat absorbed in the direct substitution. Such displacements might, he thought, take place at temperatures at which the chloride was dissociated, so that the bromine would be able to unite with the free metal. He repeated Potilizin's experiments but found no action up to 400°. Potilizin in answer to Berthelot repeated his previous

experiments, and further varied the mass of the bromine employed. He used sealed vacuous tubes, heating them at 400—515° or at 300—315°, and found that the chlorine displaced varied with the mass of the bromine, but at a given limit increase in the amount of bromine or of the temperature did not affect the quantity of chlorine displaced. He pointed out that the interaction was not in entire accordance with Berthelot's principle of maximum work, but that it depended partly on this principle and also on the atomic weight, mass, valency and temperature of the interacting bodies. Berthelot attempted to reconcile Potilizin's statements with his principle by assuming that intermediate compounds—metallic perbromides and chlorobromides together with bromine chloride—were formed and dissociated. In the light of such a supposition he considered the displacement of chlorine by bromine if the latter is present in excess, and the small displacements if the two are in equivalent proportions, to be in accordance with the provisions of thermal chemistry.

In answer, Potilizin stated that he verified the formula $\frac{A}{pE^2} = a$ constant, in the case of 14 chlorides, also in the case of nickel and cobalt. He denied that intermediate compounds could exist at the temperature of the interaction, and thought the cause of the interaction must be sought for "in the intramolecular conditions of the bodies; being probably dependent on the varying rates of the molecules."

No further work appears to have been done on the subject, and in order to test the validity of the law stated by Potilizin the following experiments were instituted:—

An amount of bromine equivalent to about 1 gram of anhydrous chloride was sealed off in a small glass bulb, and a quantity of the salt, exactly equivalent to the quantity of bromine taken, was weighed out into another bulb, and the two were placed in a piece of glass tubing closed at one end. At about 6 inches from the closed end the tube was thickened in the flame and drawn out into a thick capillary. Beyond this point it was drawn out and bent so as to be evacuated by the Sprengel pump. When the exhaustion was complete the tube was sealed up by directing a blowpipe flame on to its capillary portion; the point was then annealed and the tube allowed to cool. The bromine bulb was next broken and the chloride distributed as uniformly as possible over the inside of the tube, in order to expose it most advantageously to the action of the bromine. By means of an air-bath the tubes were heated to about the boiling point of mercury in some cases and to about 450° in others.

After heating, the tubes were freed from any adherent oxide of iron due to contact with the iron tubes of the bath, by immersion in

warm chlorhydric acid, washed, dried, opened by means of a hot wire on a piece of glazed paper, and heated at 120° till the free bromine was expelled and the weight constant. Lastly, the contents of the tubes were washed out and the empty tubes weighed. From the increase in weight of the chloride taken the amount of bromine substituted and hence the chlorine displaced could be calculated. The results of the experiments carried out in this way are given in the subjoined table. Chlorides marked with the same letter were heated simultaneously :—

It will be seen that only on one occaion—in the case of silver chloride—was a number got in anything like agreement with the figures demanded by Potilizin's law. In all other cases, the amount of chlorine displaced was considerably less than that required by the law. The table, however, shows, that although the amount of chlorine displaced stands in no definite relation to the atomic weight of the metal in the chloride used, yet in all cases most chlorine is displaced from the chloride of highest molecular weight when several are heated simultaneously. Further, in all cases with the exception of silver chloride, the longer the time of heating, the more chlorine was substituted, and hence it might be thought that if the time of heating were sufficiently prolonged, a limit would be reached. On the other hand, in no instance was the amount of chlorine displaced in any one chloride proportional to the time of heating; even after heating sodium chloride for 120 hours scarcely half the quantity demanded by Potilizin's law was substituted. In the only case in which Potilizin gives definite data, viz., in the case of barium chloride, the percentage of chlorine displaced was 7·78 on heating from two to six hours at 400°, whereas we obtained only 4·8 on heating for 17 hours at about 450°.

The authors consider that these observations altogether disprove the validity of Potilizin's law of displacement.

Chloride used.	Temperature of bath.	Time of heating.	Percentage of chlorine replaced.	Percentage given by the law.
(*a*) NaCl	about 350°	8 hours	0·5	5·5
(*b*) NaCl	,, 450	14 ,,	1·84	5·5
NaCl	,, 450	120 ,,	2·6	5·5
(*a*) KCl	about 350°	8 hours	2·7	9·78
(*b*) KCl	,, 450	14 ,,	3·4	9·78
(*a*) AgCl	about 350°	8 hours	23·3	27·28
(*b*) AgCl	,, 450	14 ,,	24·7	27·28
AgCl	,, 350	8 ,,	27·42	27·28
(*c*) $SrCl_2$	about 450°	17 hours	1·3	5·2
(*c*) $BaCl_2$	about 450°	17 hours	4·5	7·78
(*c*) $PbCl_2$	about 450°	17 hours	5·0	12·4

13. "A Gasometric Method of Determining Nitrous Acid." By Percy F. Frankland, Ph.D., B.Sc., F.I.C.

The method is based on the well-known interaction of urea and nitrous acid. The author evaporates a definite volume of the solution containing the nitrite to dryness in a small beaker on the water-bath, the residue is then dissolved in a few c.c. of hot distilled water, and transferred along with an excess of urea to a tube standing over mercury. Dilute sulphuric acid is then admitted, whereupon an evolution of nitrogen and carbonic anhydride takes place. The reaction is found to be complete in 15 minutes. An excess of a strong solution of pure caustic soda having been admitted into the tube to absorb the carbonic anhydride, the residual nitrogen is transferred to a gas-apparatus and measured.

The method was found to yield very satisfactory results.

The method was also employed for determining nitrites in the presence of nitrates and ammonia: the nitrate was destroyed by evaporating one portion of such a mixture with excess of ammonium chloride, and the nitric acid in the residue was then determined by the mercury method; whilst another portion was evaporated with an excess of pure caustic soda—to prevent the destruction of the nitrite by the ammonia present—and in the residue the nitrous acid was determined by the urea method.

14. "The Action of some Specific Micro-organisms on Nitric Acid." By Percy F. Frankland, Ph.D., B.Sc., F.I.C.

The author has investigated the behaviour, when grown in nutritive

solutions containing nitrates, of a number of micro-organisms obtained from air and water, and cultivated in a state of purity. Of 32 different forms so examined, 16 or 17 were found to reduce the nitrate to nitrite more or less completely, whilst the remainder were quite destitute of this power. The behaviour of the various organisms was not altered in this respect by excluding air from the solutions in which they were cultivated. In a number of cases the changes taking place in the condition of the nitrogen were followed quantitatively. In some cases ammonia made its appearance in the solutions, but by quantitative experiments it was found that this ammonia was due to the decomposition of peptone, which was the only other nitrogenous ingredient besides the nitrate in the cultivating medium employed. A number of special experiments were made with two micro-organisms, *Bacillus ramosus* and *B. pestifer*, which powerfully reduce nitrates to nitrites, and which also give rise to the appearance of ammonia in the peptone-culture-fluid. In these experiments it was found that the nitrite produced in a given time was augmented by increasing the organic matter, peptone and sugar present in the solution, and that the peptone was much more potent in effecting this increase than the sugar. It was further found that the ammonia generated in these experiments was increased by raising the proportion of peptone to sugar, and diminished by increasing the proportion of sugar to peptone.

In nearly all cases in which partial or total reduction of nitrate to nitrite had taken place, the sum of the nitrogen as nitrate and nitrite in the fermented solution was practically identical with the nitrate in the original unfermented solution; whilst in those cases in which no reduction to nitrite took place, the nitrate in the solution remained practically unaffected by the growth of the micro-organisms. In one case, however, it was found that an organism, *B. aquatilis*, which does not reduce nitrates to nitrites, caused by its growth the disappearance of a considerable proportion of nitric nitrogen, the deficiency not being accounted for by the small proportion of ammonia which was generated in the solution. It is pointed out how this difference in reducing power may in certain cases be of great value in distinguishing between micro-organisms morphologically very similar.

15. "The Action of Phosphorus Pentachloride on Salicylaldehyde." By Charles M. Stuart, M.A.

The author finds that phosphorus pentachloride converts salicylaldehyde into the phosphate of dichlororthocresol, $PO(O{\cdot}C_6H_4{\cdot}CHCl_2)_3$, and not into dichlororthocresol, as stated by Henry (*Ber.*, 1869, 135).

Dichlororthocresylic phosphate is not altered by boiling with potassium hydroxide solution. By the action of phosphorus penta-

chloride on orthomethoxybenzaldehyde, orthomethoxybenzal chloride. $C_6H_4(OCH_3)\cdot CH_2Cl_2$, is obtained; this is readily reconverted by the action of warm water into the aldehyde from which it was formed.

16. "Some interactions of Nitrogen Chlorophosphuret." By Ward Couldridge, B.A.

The paper is chiefly devoted to the description of experiments on the action of amines on nitrogen chlorophosphuret, $P_3N_3Cl_6$, the compound which results on heating together phosphorus pentachloride and ammonium chloride; the small yield obtained by this process is attributed by the author to the formation of phospham, $P_3N_3(NH)_3$, by the action of ammonia on the chlorophosphuret. He finds that the compound $P_3N_3(NH\cdot C_6H_5)_3$, which Hofmann prepared by treating the chlorophosphuret with aniline, is not altered by heating with muriatic acid at 150°, but that at 250° it is resolved into phosphoric acid, ammonium chloride and aniline chlorhydride. By the action of orthotoluidine, a compound of the formula $P_3N_3(NH\cdot C_6H_4\cdot CH_3)_6$ was obtained, and similar compounds were prepared from phenylhydrazine and piperidine. Attempts to displace the chlorine by cyanogen were unsuccessful, and experiments with sodium and with zinc ethide also gave negative results.

17. "Action of Alcohols on ethereal salts in presence of small quantities of Sodic Alkylate." By T. Purdie, Ph.D., B.Sc., Professor of Chemistry in the University of St. Andrews, and W. Marshall, B.Sc.

The addition of a minute quantity of sodic alkylate to a mixture of an alcohol and an ethereal salt induces an extensive interchange of alkyl radicle between the two substances. The authors having examined the interaction in the case of a number of ethereal acetates and alcohols of the $C_nH_{2n+1}OH$ series, find that a much greater interchange occurs when the alcohol of complex radicle acts on the ethereal salt of simple radicle than in the converse interaction. The numerical results obtained indicate that, excluding the methyl radicle, the affinity of the alkyl radicles for the hydroxyl-oxygen of the acid, as measured by the interaction under consideration, increases with increasing complexity of the alkyl radicle; but that with regard to the methyl-radicle its affinity is greater than that of the ethyl and less than that of the amyl radicle.

18. "Note on the densities of Cerium Sulphate Solutions." By B. Brauner, Ph.D.

The author has determined the densities of solutions of the anhydrous and of the hydrated salt, and finds that the values are identical for solutions of equal concentration.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Accidents in Mines, by F. A. Abel; with an Abstract of the Discussion upon the Paper. London 1888. From the Author.

Die chemische Kräfte, von G. A. Hagemann; aus dem Dänischen übersetzt, von T. Knudsen. Berlin 1888 (Pamphlet). From the Author.

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At the next meeting on March 2nd, the following paper will be read:—

"The origin of colour and the constitution of colouring matters generally:" by Professor Armstrong.

HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY, ST. MARTIN'S LANE.

ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 49. Session 1887–88.

March 1st, 1888. Mr. William Crookes, F.R.S., President, in the Chair.

Messrs. Lewis Walter Hawkins and B. Henry Gerrans, Junr., were formally admitted Fellows of the Society.

The list of Office Bearers nominated by the Council to be balloted for on March 28th was read.

Certificates were read for the first time in favour of Messrs. Joseph Cowper, St. Andrew's Place, Penrith; Eugene MacSwiney, 18, Lower Kevin Street, Dublin; Henry John Palmer, 126, York Road, Bedminster, Bristol; John Cecil Watson, The Rhyddings, Oswaldtwistle, near Accrington; Thomas Howell Williams, 58, Lady Margaret Road, St. John's College Park, N.W.

The following Papers were read:—

19. "The origin of colour and the constitution of colouring matters." By Henry E. Armstrong.

The majority of compounds, especially those of carbon, are colourless; and in the case of elements whose compounds are invariably coloured, the greatest diversity of colouring is often noticeable among the several compounds of one and the same element—as in that of chromium or manganese, for example: it is therefore clear that colour is in a high degree conditioned by special forms of intramolecular structure, and consequently that any attempt to determine the "origin of colour" must be based on a knowledge of the structure of coloured matters. For this reason it has become possible only within recent years to discuss the relation between colour and constitution. The author first gives an account of what has already been done in

this direction, and refers to Graebe and Liebermann's paper on "The connexion between constitution and colour in the case of organic compounds" (*Ber.*, 1868, 106); and to that of O. N. Witt—"Zur Kenntniss des Baues und der Bildung färbender Kohlenstoffverbindungen" (*ibid.*, 1876, 522). Graebe and Liebermann laid down the rule as of universal application that, excluding coloured metallic salts of colourless organic acids, all coloured organic compounds which have been put to the test are decolorised by reducing agents (quinones, azobenzene, nitro-compounds, &c.); and from this they inferred that colouring matters either contain elements with incompletely saturated affinities, or certain of the atoms are present in more intimate association than their retention in the molecule necessitates. Notwithstanding the change in our views of the constitution of quinone, Graebe and Liebermann's conclusions appear still to be accepted, although if Fittig's contention that the quinones are diketones be correct, their conclusion that the colour of the quinones is conditioned by the intimate union of the oxygen-atoms obviously does not apply. Witt formulated the conclusion that the tinctorial nature of aromatic compounds is the consequence of the presence together of a colour-giving or *chromophoric* group, such as NO_2, CO, N : N, and of a salt-forming group—either OH or NH_2. This chemist directed his attention almost exclusively to the consideration of the nature of compounds possessed of tinctorial properties as distinct from mere coloured substances or pigments. The origin of colour, however, is presumably traceable to similar causes in both classes of compounds, while the property of acting as a dye may conceivably depend on peculiarities which stand in no relation to those which are causative of colour; this is an important question to determine.

The dominant idea on which the argument in the paper is based is illustrated by the author by comparison of the unsaturated hydrocarbons with the paraffins. In the paraffins, which are singularly inert compounds and all but colourless even in the infra-red and ultra-violet regions of the spectrum, the carbon-atoms are united only by single affinities, and the remaining affinities are engaged by *monad* atoms; the unsaturated hydrocarbons are not only more reactive than the paraffins, but the beginnings of colour are manifest in them if examination be made in the regions above and below the visible spectrum. The latter are conventionally represented by formulæ in which the carbon-atoms appear as united by two or three affinities of each, typified by straight lines or dots; these formulæ apparently serve to indicate that the value of a "double bond" is twice, and that of a "treble bond" thrice that of a "single bond," and there can be little doubt that this has long been tacitly assumed, although such a doctrine may not actually have been taught. But within recent

years the idea has found favour that "affinity has direction"; v. Baeyer especially has availed himself of this hypothesis in his discussion of the differences in stability of various types of closed chain hydrocarbons. The author would apply it to polyad-atoms generally; and in formulating compounds in which such atoms are united by more than single affinities, would represent the polyad atoms as united by curved lines in order to suggest that the affinities are under strain in consequence of their being free to act only in certain directions. In the paper, the author cites a large number of cases among inorganic compounds which he thinks afford evidence that the production of colour is dependent on special modes of atomic arrangement, and particularly on such modes of arrangement as involve the existence of a condition of strain in the resulting system, due probably to peculiarities in the affinity relationships of the constituent elements of the system which prevent complete mutual neutralisation of the affinities. The occurrence of colour therefore is more frequently than not concomitant with a high degree of reactivity, the coloured compound being usually one of "high potential" or slight stability.

Among carbon compounds there is no instance of a hydrocarbon being coloured, giving the term its conventional meaning; and omitting nitro-compounds, there are very few exceptions to the rule that derivatives of hydrocarbons containing only monad radicles are colourless; the exceptions, moreover, are of a very noteworthy character, being either *central* derivatives of anthracene, *i.e.*, compounds formed by displacement of the hydrogen-atoms of the central nucleus of anthracene—which although not coloured is significantly fluorescent; or the monad radicle contains at its origin a radicle such as CO. A number of illustrations are given in illustration of this statement. Attention is then drawn to the quinones and their derivatives, Fittig's ketone formula being throughout adopted for these compounds. The author then discusses the constitution of the better known dye-stuffs, and is thereby led to conclusions which in some cases are different from those hitherto accepted.

Azo-dyes.—Liebermann's experiments on benzene-azo-betanaphthol are referred to, and also those of Zincke and Bindewald, attention being specially directed to the production by these latter chemists from alphanaphthaquinone and phenylhydrazine of benzene-azo-alpha-naphthol identical with that obtained from alphanaphthol and a diazobenzene salt. The author thinks that the general bearing of these results has escaped notice, and proposes to apply them to azo-dyes generally, formulating these as of the following types:—

$$O\subset C_6H_4\subset N\cdot NHR' \qquad HN\subset C_6H_4\subset N\cdot NHR',$$

according as they are derived from phenols or amines. The high tinctorial power of the azo-dyes would appear to meet with a more satisfactory explanation on this hypothesis than is afforded by Witt's theory, and it affords a simple explanation of the fact that no acid radicle other than OH, and only ortho- and para-hydroxy or amido-compounds are available for the preparation of azo-dyes. The cases in which this hypothesis will not apply are discussed in the paper.

Rosaniline and its congeners.—Although the formulæ usually assigned to these represent them as compounds of the quinonic type—assuming that in quinone the oxygen-atoms although in the para-position are united to each other, the idea that they are quinonic compounds which Graebe, Liebermann and Caro expressed prior to the publication of E. and O. Fischer's well-known investigation has apparently now been entirely lost sight of. The author would formulate them in the manner indicated by the following examples:—

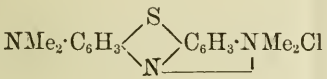
$O\subset C_6H_4\subset C(C_6H_4{\cdot}OH)_2$ — Pararosolic acid.

$HN\subset C_6H_4\subset C(C_6H_4{\cdot}NH_2)_2$ — Pararosaniline.

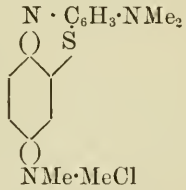
Phthaleïns.—v. Baeyer's researches are commonly held to prove that these compounds are derivatives of phthalide, $C_6H_4\left\{\begin{matrix}CH_2\\CO\end{matrix}\right\}O$. The arguments on which this conclusion is based are discussed in the paper; it is pointed out that the properties of the various compounds classed as phthaleïns are so diverse that it is desirable to more fully examine the evidence on which they are grouped together, especially as, apart from the assumption that the phthaleïns are phthalide-derivatives, there is little reason to believe that the lactides are chromophoric compounds. v. Baeyer supposes that phenolphthaleïn is formed from dihydroxytriphenylhydroxymethanecarboxylic acid by separation of the elements of water from the carboxyl and the methane hydroxyl, a lactonic anhydride being thereby produced; but if the hydroxyl of the carboxylic radicle were to separate with a hydrogen-atom of the neighbouring $C_6H_4{\cdot}OH$, a derivative of hydroxyphenyl-anthranol would be obtained. This latter constitution, however, has already been assigned to the phthalideïn isomeric with phenol-phthaleïn. The conclusion that interaction does take place in this latter manner in the formation of fluoresceïns would serve to explain the fact that orcinol ($CH_3 : OH : OH = 1 : 3 : 5$) does not yield a fluoresceïn, whereas the isomeric cresorcinol ($CH_3 : OH : OH = 1 : 2 : 4$) does, as an anthracene-derivative could only be formed from an orcinol containing two *contiguous* undisplaced hydrogen-atoms. It is possible that certain of the phthaleïns are derivatives of phenylenediphenyl ketone, $C_6H_4(COC_6H_5)_2$. The formation of triphenylmethane-derivatives from compounds of this type can easily be accounted for, as

benzil is converted by alkali into diphenylglycolic acid; and this assumption would serve to explain the formation of additive compounds with acids, such as are obtained from orcinphthaleïn, for example. It is noteworthy that the dimethanilidophthaleïn prepared from dimethylaniline is not only itself colourless, but yields colourless salts; this may be a true phthalide-derivative. Also that the diamidodiphenylphthalide which v. Baeyer prepared from diphenylphthalide and which he converted into phenolphthaleïn, when methylated yields a green compound apparently identical with the "phthalic-green" which O. Fischer prepared from dimethylaniline and which he represented as an anthracene-derivative.

Methylene-blue.—It is suggested that this also is a quinonic compound, thus :—



Bernthsen's formula.



Quinonic formula.

Other dye-stuffs and coloured compounds are considered in the paper.

Discussion.

Dr. Debus said that Dr. Armstrong had called attention particularly to the type of coloured substances. Now flowers of sulphur at $-50°$ are white; larger pieces of sulphur are nearly colourless; but on warming both forms become more and more yellow, and at $+50°$ are of an intensely yellow colour. Whatever be the type on which sulphur molecules are built up, there is not the slightest evidence that its chemical properties are changed between $-50°$ and $+50°$, or in other words that the structure of its molecules is altered. The colour of sulphur, therefore, is not dependent on its chemical type between $-50°$ and $+50°$, but on its temperature. Many similar examples can be quoted. Thus zinc oxide is white at common, and yellow at higher temperature. The influence of molar arrangement is seen in the following examples: larger pieces of silver are white, powder of silver is black; pieces of platinum grey, powder of platinum black; a sublimate of mercuric sublimate is dark brown, and powder of the same substance red. In all these cases there is no evidence that the molecular structure of the substances has undergone any change.

Professor Rücker said that if he had understood Professor Arm-

strong rightly his hypothesis was not in any way opposed to the idea that the forces between atoms acted in straight lines. If for purposes of illustration they made the crude supposition that a carbon-atom had four poles or centres of force on its surface, it was possible to conceive another atom adhering to one of the poles, or to a point on the surface half way between two of them. The heat of combination, the stability of the compound and so forth, would depend on the position assumed by the second atom relatively to the poles, but no single pole would have done the maximum amount of work which the attractions it exerted could perform on the atom until the latter finally adhered to it. In other positions there would therefore be a certain amount of "residual affinity." A position of more or less stable equilibrium might be found in which an atom combining with others was under the influence of a resultant force which was not equal to the sum of its individual components, and he believed that it was ideas of this kind which Professor Armstrong's notation was intended to convey.

As regards the question whether colour was due to the internal arrangement of the molecule, absorption was ordinarily attributed to vibrations set up among the atoms of which each molecule was composed.

He thought that attempts such as that embodied in the paper to connect the physical properties of substances with the molecular constitutions were necessary before any further attempt was made to frame a mechanical theory by which the connection should be explained.

Professor G. C. Foster referred to Professor Armstrong's remark, near the beginning of his paper, that, in the discussion of the coloration of bodies, their behaviour towards the invisible ultra-red and ultra-violet parts of the spectrum could not be separated from their behaviour towards the visible rays. In his opinion this remark was of fundamental importance. It appeared to him that the real question raised by Dr. Armstrong was whether a definite relation could be traced between chemical composition or chemical structure and the existence and position of absorption-bands in the spectrum of the transmitted radiation. The presence or absence of coloration, as it could be judged of directly by the eye, gave no conclusive answer to this question, for, as Professor Dewar had just reminded them, a substance might be as colourless as water, and still exert strong absorption in the ultra-red, or, as in some of the substances examined photographically by Professor Hartley, it might have strongly marked absorption in the ultra-violet. But, more than this, a body might exert selective absorption within the visible spectrum, but if it happened to absorb two complementary colours it would be judged

of by the eye as though it were destitute of selective absorption altogether. The subject, therefore, seemed to him to involve a systematic study of absorption-spectra.

Dr. Morley saw great difficulty in applying to inorganic compounds Dr. Armstrong's hypothesis that the less stable bodies were the more highly coloured, and instanced the yellow and red mercuric iodides, the red iodide being the more stable at ordinary temperatures.

Mr. A. G. Green remarked that, as he understood, Dr. Armstrong considered the colour of organic colouring matters to be due to the unsaturated affinities or high potential of the quinone type to which these compounds can all be referred. Now he believed Dr. Armstrong regarded water as both an unsaturated and a coloured body, so, applying the same argument, why should not all aromatic compounds capable of being referred to the water type be coloured, or, at any rate, such as have sufficient molecular weight?

Dr. Armstrong, in reply, referring to Professor Foster's remarks, said that there was great difficulty in discussing colour, owing to the want of any agreement as to a colour scale, which made it impossible to compare effects produced in different regions of the spectrum; it would undoubtedly be necessary ultimately to take into account the absorption effected in the regions beyond the visible: at present, however, there was far too little information at our disposal for this purpose, but he believed that the same principles would apply in the main. In the course of the discussion he had been asked for explanations of matters which he did not pretend to explain; he did not claim that what he had said was particularly novel, but it did appear to him that it was of importance to group together the facts, and the conclusions with regard to the character of coloured compounds in general at which he had arrived appeared to be of significance.

20. "Researches on Chromorganic Acids. Part II. Certain Chromoxalates of the Red Series." By Emil A. Werner.

The author has further studied Croft's red salt, prepared by the interaction in aqueous solution of potassic dichromate and oxalic acid in the proportion of 1 to 7 molecules. Crofts gave to it the formula $K_2Cr_2(C_2O_4)_4 \cdot 12OH_2$, but the author finds only 10 OH_2. Six of the 10 molecules of water are readily expelled, the red salt becoming bluish-grey; but the remainder are removed with difficulty, complete dehydration being effected only at about 300°. The dehydrated compound is of a deep-green colour. It is proposed to represent the red salt by the formula $Cr_2(OH)_2 \left\{ \begin{matrix} (CrO_2 \cdot OK)_2 \\ (CrO_2 \cdot OH)_2 \end{matrix} \right.$. Several derivatives of the salt are described in the paper.

21. "Note on Benzyldithiourethane." By A. E. Dixon, M.D.

Several of the monalkyl substituted dithiourethanes are known. The following is a short account of a new member of the series. It was prepared early in 1887 in Professor A. W. Hofmann's laboratory.

Benzyl mustard-oil was sealed up in a tube with a quantity of ethyl mercaptan slightly in excess of that required by the equation—

$$CS:N\cdot CH_2\cdot C_5H_5 + C_2H_5SH = CS(SC_2H_5)NH\cdot CH_2\cdot C_6H_5.$$

The mixture was heated for five hours at a temperature of 120°, the tube opened, and the contents heated for a short time on the water-bath in order to drive off the excess of mercaptan. After standing for a few days the liquid solidified to a crystalline mass: this was dissolved in alcohol and the alcohol allowed to spontaneously evaporate. By this means large transparent and perfectly colourless prismatic crystals were obtained, over 3 cm. in length, nearly $\frac{1}{2}$ cm. broad, the yield being over 80 per cent. of the theoretical.

The substance is insoluble in water, moderately soluble in ether, benzene and ligroïn, and extremely soluble in alcohol and bisulphide of carbon. The alcoholic solution is instantly desulphurised on warming with alkaline lead solution.

The crystals melt at 47° without decomposition; on heating more strongly the substance decomposes into mustard-oil and mercaptan. On analysis, the following data were obtained:—

0·2545 gram burnt with $PbCrO_4$ gave 0·5329 CO_2 and 0·1449 H_2O; or C = 57·10 per cent., H = 6·32 per cent.

0·2308 gram fused with $Na_2CO_3 + KClO_3$ gave 0·5003 $BaSO_4$, or S = 29·80 per cent.,

which agrees with the formula $C_{10}H_{13}NS_2$.

	Theory.		Experiment.		
C_{10}	119·7	56·82	57·10	—	—
H_{13}	13·00	6·17	6·32	by diff.	—
N	14·01	6·65	—	6·78	—
S_2	63·96	30·36	—	—	29·80

At the next meeting, on March 15th, the following papers will be read:—

"The Nature of Solutions as elucidated by the Heat evolved on Dilution. Part I. Calcium Chloride." By S. U. Pickering.

"The Action of Isothiocyanates on Aldehyde-ammonias." By A. E. Dixon, M.D.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 50. Session 1887–88.

March 15th, 1888. Mr. William Crookes, F.R.S., President, in the Chair.

Messrs. Charles Francis Townsend, John Frederick Hayes and D. A. Nagel were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Ludwig Claïsen, 6, Sopheinstrasse, München; William Henry Dodd, 8, Kempson Road, Fulham, S.W.; John Gill, Gwealhellis, Helston, Cornwall; Frederick Preston de Jong, South Shore, Blackpool; Thomas Enraght Lindsay, B.A., Royal Medical College, Epsom; John George Taylor, 12, Ernest Street, Jarrow-on-Tyne; James Woodward, The Laboratory, Somerset House, W.C.

The following were duly elected Fellows of the Society:—Messrs. Alfred Chiddy, Thomas Ashcroft Elwood, Harold Nicolai Faber, James H. Gardner, James Hart, C. Millard King, Vivian Byam Lewes, Charles E. Munroe, Frederick G. Ruddock, H. Belcher Thornton, Thomas Edward Towerson, Herbert Trewby, Edward Arthur Wates.

The following Papers were read:—

22. "The Nature of Solutions as elucidated by the heat evolved on their dilution. Part I. Calcium Chloride." By S. U. Pickering.

The data afforded by the experiments of Berthelot and Thomsen being insufficient to determine the nature of the action which takes place on diluting aqueous solutions, the author has undertaken an elaborate examination of the question, selecting calcium chloride and nitrate as subjects of study.

A new form of mixing calorimeter has been devised, consisting of

an oval platinum beaker, divided into two compartments by means of folding doors; this apparatus secures the identity of the temperatures of the two liquids before mixing, and obviates a dependence on the accurate comparison of two thermometers. The heat capacity of the solutions was determined by means of two equal resistance coils through which the same current flowed and which heated simultaneously a known weight of water and of the solution under examination.

Experiments with the weaker solutions were conducted in the mixing calorimeter; the stronger solutions were treated like solids, the heat of their dissolution in a large quantity of water being determined. The strongest solutions dealt with were supersaturated, containing only 5·7 H_2O; the weakest one contained 1400 H_2O, or 0·4 per cent. $CaCl_2$.

Various methods of graphic representation were examined, but the only one which led to satisfactory results was the plotting of the heat of dissolution (in an infinite amount of water) of 100 grams of solutions of various strengths against the percentage composition of these solutions.

The results form a curve of great regularity, but this regularity is only apparent; on differentiation a series of independent curves are obtained, each of which on further differentiation gives a straight line. (The lines are straight within experimental error, but they all exhibit an inclination towards a curved form, which suggests the possibility of the action being even more complicated than is here shown.) Neither these straight lines nor the first differential curves meet at the points of change when produced. A second differentiation being necessary to reduce the original curve to straight lines, it follows that the action is represented by the equation: Heat of dissolution $= A + \alpha p + \beta p^2 + \gamma p^3$, p being the percentage composition, and the other letters constants.

Owing to the multiplicity of the breaks and the smallness in the percentage difference corresponding to each additional H_2O, the case is one of extreme difficulty, and the exact position of the breaks is in some instances a matter of uncertainty. To obtain confirmatory evidence the densities of the various solutions were examined; the curve by which they are expressed split up on differentiation into a series of straight lines, as in the cases examined by Mendeléef, and the points at which the breaks occur in the curve correspond in every case with those occurring in the heat curve, and, moreover, corresponded as accurately as can be expected with definite molecular proportions of water. The breaks are as follows :—

In heat curve.	In density curve.	Mean.	Composition.
50·84 p. c. $CaCl_2$	— p. c. $CaCl_2$	50·84 p. c.	$CaCl_2,6H_2O$ = 50·66 p. c. $CaCl_2$.
45·73 ,,	46·62 ,,	46·18 ,,	$CaCl_2,7H_2O$ = 46·81 ,,
43·46 ,,	43·10 ,,	43·28 ,,	$CaCl_2,8H_2O$ = 43·51 ,,
38·52 ,,	38·52 ,,	38·52 ,,	$CaCl_2,10H_2O$ = 38·12 ,,
32·70 ,,	31·8 ,,	32·25 ,,	$CaCl_2,13H_2O$ = 32·15 ,,
26·35 ,,	25·85 ,,	24·10 ,,	$CaCl_2,18H_2O$ = 25·50 ,,
17·52 ,,	18·75 ,,	18·13 ,,	$CaCl_2,28H_2O$ = 18·04 ,,
6·51 ,,	7·40 ,,	6·95 ,,	$CaCl_2,90H_2O$ = 6·41 ,,
0·42 ,,	0·49 ,,	0·45 ,,	$CaCl_2,1400H_2O$ = 0·44 ,,

It having been already shown before this Society that the variation in electrical conductivity and the density of sulphuric acid on diluting with water unanimously prove the existence of certain hydrates in solution, as the results of the study of the densities and the thermal changes are shown to be equally unanimous in the case of calcium chloride solutions, the author is of opinion that there can therefore no longer be any reasonable doubt but that solutions do in reality consist of such hydrates, and holds that any theory of the nature of solutions which ignores their existence must be rejected absolutely and for ever.

Discussion.

Dr. Armstrong said that although personally he was prepared to agree with Mr. Pickering in his conclusions, he thought that probably very many chemists would hesitate to accept Mendeleéf's explanation until evidence of the existence of definite hydrates in solution had been obtained by discussing the dependence of a greater variety of properties on composition: the fact that the same results were arrived at by discussing heats of dissolution and densities in the case of calcium chloride was therefore a most valuable addition to our knowledge. Mr. Pickering had incidentally raised the question whether the curves actually met at points corresponding to definite hydrates—the observations hitherto made were not sufficiently numerous to determine this, but judging from the results arrived at by Mr. Crompton in discussing electrical conductivity values, they probably did not; it was necessary, in fact, to prolong the curves in order to determine the points of intersection. The curves began to change direction at some distance on either side of the points corresponding to particular hydrates: this probably was due to the fact that in a given solution, even before sufficient or more water is present to form a hydrate A, a varying quantity of a hydrate B richer in water, or of a hydrate C containing less water, according to circumstances, is formed. If this be the case, it is to be expected that if sufficiently

numerous observations are made at different temperatures, it will be possible by Mendeléeff's method to determine not only the nature of the hydrates present, but also within certain limits the extent to which dissociation has set in.

Mr. Crompton pointed out that Professor Pickering's results again showed the necessity in this and kindred problems, of no longer assuming a curve to be continuous simply on account of its presenting a smooth and regular appearance: on analytical treatment such an apparently continuous curve might break up and prove to be discontinuous and made up of a series of curves, as in the present case. The apparent regularity of Thomsen's heat of dissolution curves was largely owing to the method of representation adopted, and want of a sufficient number of observations in most cases prevented an analysis of his results. The method hitherto pursued of merely measuring the heat evolved at points where breaks in the curve might be expected to occur, was also hardly calculated to lead to the detection of such breaks, as these would best be discovered when the directions of the intermediate curves had been determined.

23. "The Action of Thiocyanates on Aldehyde Ammonias." By A. E. Dixon, M.D.

The author describes the products of the interaction of benzylthiocarbimide with aldehyde-ammonia and valeraldehyde-ammonia; of ethyl-, allyl-, phenyl- and orthotolylthiocarbimide with aldehyde-ammonia; and of phenylthiocarbimide with valeraldehyde-ammonia. They apparently may all be regarded as derivatives of the compound which Nencki obtained from thiocarbamide and aldehyde-ammonia; this the author represents as a closed chain compound of the formula $CS<^{NH\cdot CH(CH_3)}_{NH\cdot CH(CH_3)}>NH$. It is pointed out that R. Schiff, by operating in practically the same way, obtained compounds differing in composition from those prepared by the author; and it is suggested that Schiff may not have prepared the substances in a sufficiently pure state for analysis.

24. "Carboxy-derivatives of Quinone." By J. U. Nef.

The author originally undertook the preparation of quinonetetracarboxylic acid, $C_6(O_2)(CO_2H)_4$, in order to compare it with croconic acid, which has the same percentage composition, the constitution of which was undetermined at the time when the experiments were commenced; the results are entirely confirmatory of the conclusion that croconic acid is not a benzene-derivative.

All attempts to oxidise durenequinone, $C_6(O_2)(CH_3)_4$, proving unsuccessful, durylic acid, $C_6H_2(CH_3)_3{\cdot}COOH$, was converted into dinitrodurylic acid, from which by oxidation with permanganate the tetracarboxy-acid was prepared; and ultimately this was converted into quinonetetracarboxylic acid. The preparation both of these compounds and of a variety of intermediate products and derivatives and their properties are fully described in the paper; a portion of the results have already been published in the *Annalen* (**237**, 1; *c.f. Chem. Soc. Abs.*, 1887, 255).

Ethylic diamidotetracarboxylate, from which the quinone carboxylate was obtained by oxidation with nitric acid, closely resembles the allied diamidoterephthalate studied by v. Baeyer; on reduction it is converted into a hexahydrobenzene-derivative—ethylic paradiketohexamethylenetetracarboxylate, $CO<\begin{matrix}CH(CO_2Et){\cdot}CH(CO_2Et)\\CH(CO_2Et){\cdot}CH(CO_2Et)\end{matrix}>CO$. Ethylic quinonetetracarboxylate has a yellow colour, but is odourless; it sublimes readily without decomposing, and is scarcely acted on even by prolonged heating with concentrated nitric acid. Ethylic quinoltetracarboxylate, $C_6(OH)_2(CO_2Et)_4$, prepared by reducing the quinone with zinc-dust and acetic acid, is a very remarkable substance: on further reduction it is converted into the paradiketohexamethylenecarboxylate, which most closely resembles Herrmann's ethylic succinosuccinate; it exists apparently in three distinct modifications, only two of which, however, have been studied—the one modification is green and crystallises in needles; the other is pale yellow and crystallises in plates; after fusion and cooling, the former appears dark yellow, the latter bright yellow. If either modification be separately dissolved in carbon bisulphide, a solution is obtained from which the two substances crystallise out together; the solution has the same colour and the same absorption-spectrum whichever modification be dissolved. In the paper the author calls attention to a number of similar cases of dimorphism. Quinoltetracarboxylic acid has a pale-yellow colour, and yields yellowish metallic salts which exhibit a characteristic green fluorescence; it is not converted into quinonetetracarboxylic acid by oxidising agents: a similarly remarkable resistance to conversion into the corresponding quinone-derivative has been observed by the author in the case of quinolcarboxylic acid.

25. "The Action of Acetone on Ammonium Salts of Fatty Acids in presence of Dehydrating Agents." By S. Ruhemann and D. J. Carnegie.

As chief product of the interaction of acetone and ammonium

acetate in presence of phosphoric anhydride, the authors have obtained a base of the formula $C_9H_{15}N$, which they find is identical with the dehydrotriacetonamine discovered by Heintz. On treating the compound $C_9H_{15}N$ with bleaching-powder solution, it gave an unstable chlorinated derivative; on submitting this to the action of alcoholic potash a liquid (b. p. 78—79°) was obtained which the authors regard as a new isopropyl alcohol hydrate of the formula $C_3H_5O{\cdot}OH_2$. The same substance was produced on substituting formate and butyrate for the acetate: hence it follows that only the ammonia of the salt is concerned in the formation of the base.

26. "A Method of Estimating Nitrites either alone or in presence of Nitrates and Chlorides." By T. Cuthbert Day.

The method consists in saturating the solution containing the nitrite with solid ammonium chloride, boiling the mixture in a suitable apparatus, after removal of the air by carbonic anhydride, and collecting and measuring the nitrogen evolved; interaction takes place according to the equation $NO_2K + NH_4Cl = KCl + 2OH_2 + N_2$, hence the quantity of nitrite present in the substance under analysis is calculated from half the volume of nitrogen obtained.

The Anniversary Meeting will take place on Wednesday, March 28th, at 8 P.M. The President will deliver an Address on Elements and Meta-elements.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 51. Session 1888–89.

March 28th, 1888. Annual General Meeting. Mr. W. Crookes, F.R.S., President, in the Chair.

The President delivered an address, of which the following is an abstract:—

The number of Fellows of the Society is 1571, of whom 37 are honorary foreign members. Eleven Fellows have died during the year:—Prof. C. L. Bloxam; J. B. Boussingault (foreign member); Patrick Duffy; J. J. Field; A. M. Graham; Prof. T. S. Humpidge; James Millar; A. Muter; H. H. MacMunns; W. B. Ritchie; Dr. Arthur Phillips; G. B. Sweeting; and A. E. Wilson.

11 Fellows have withdrawn:—L. M. Deane; H. W. Eve; G. F. Dowdeswell; G. Gladstone; Hugh R. Mill; Ed. Packard; T. A. Rickard; B. M. F. Rogers; C. A. Stitt; J. E. Tuit; and J. C. Wright.

30 Fellows have been removed on account of arrears:—Harry Allen; A. W. Bickerton; G. E. Barker; Dr. H. C. Bartlett; Benjamin Browning; G. E. Basu; C. N. Betts; T. J. Barr; R. D. Courtney; Thomas Donnelly; W. T. H. Elsey; H. W. Fenner; Wm. Fox; Thos. Gibbs; G. A. George; Chas. Gillett; W. E. Heathfield; E. A. Harris; Edwin Lapper; R. T. Matthews; Alexr. Noble; Arthur Ness; O. Davies Owen; J. A. Ogilvie; Thos. Palmer; Matthew Percy; J. Schweitzer; Sidney Trivick; Rev. W. G. Whittam; and Wm. Wilson.

116 Fellows have been elected during the year, including 7 honorary foreign members.

There are 88 original Papers, occupying 871 pages, in the 1887 volume of the Transactions, as against 85 Papers of 865 pages in the 1886 volume. The Abstracts this year occupy 1159 pages, as against 1088 in 1886. The number of Abstracts is 2277, as against 2164—the average of the five years preceding. 108 Papers have been communicated to the Society during the session—10 fewer than in the

previous session ; but not a few have been of exceptional interest and value, a number of important questions having been brought forward for discussion: this view is confirmed by the fact that the Transactions contain a greater number of Papers than in any previous year.

The Longstaff Medal has been awarded by the Council to Dr. W. H. Perkin, F.R.S., in recognition of the importance of his researches on the magnetic rotatory polarisation of compounds in relation to their chemical constitution. The President said that he was sure the Society would cordially join with him in congratulating Dr. Longstaff that, although he is near the eve of his 89th birthday, he is still hale and hearty, and in expressing the hope that he may long be spared. In bestowing the medal he remarked:—

"It is not often that an opportunity such as that which has fallen to Dr. Perkin's lot is so fully made use of, and that one who has been engaged in industrial pursuits undertakes a research of such magnitude as that of which Dr. Perkin first gave an account to the Society in 1884 (Trans., pp. 421—579), and which it is known has since wholly engaged his attention."

The cost of publishing the Transactions and Abstracts during the past year has been no less £2116. It is to be expected. said the President, that as the number of Papers offered to the Society multiplies—as it surely will—and as the number of Papers to be abstracted augments, the cost will become even greater. Our publication is of such supreme importance to chemical science in this country, that the Society is not likely to shrink at necessary expenditure. But he felt impelled to refer to a question which ere long must be seriously considered, not only by us, but by scientific societies generally, viz., how far it is desirable that the same Paper should be published in more than one Journal. Our bye-laws only provide that authors shall not be at liberty, save by permission of the Council, to publish in English the papers they have communicated to the Society until such Papers, or abstracts of them, have either appeared in the Journal or have been returned to the writer. It must be taken for granted in this time of culture that a paper published in English, French, or German is thus made known to the entire scientific world, and, in the case of a Paper published in full in one of these three languages, it is unnecessary to give triple repetitions; an abstract of the essential facts, observations and conclusions would be all sufficient. Some such curtailment will probably find favour, not only as a means of diminishing the cost of publication to individual societies, but also because it will put an end to the grievance undoubtedly felt by subscribers to scientific journals, of paying more than once for the same set of facts.

With perhaps two incomplete exceptions, we have not witnessed

during the past session the dawn of any epoch-making, far reaching discovery which opens out new and tempting prospects of truth. The two exceptions are the researches of Krüss and Nilson, and the mathematical discussions of spectra by Professor Grünwald; these latter seem at least to foreshadow the conclusion that hydrogen, oxygen, carbon and magnesium are not simple bodies but compounds, and if the phenomena admit of no other explanation, and if no unexpected source of error be detected, we may consider ourselves to be within measurable distance of a truly new chemistry. But here time must decide.

The President next drew particular attention to the tardy justice accorded to Mr. J. A. R. Newlands by the award of the Davy Medal of the Royal Society; and he referred to the action taken by Professor Frankland in bringing about the recognition of Mr. Newlands' claim to be the discoverer of the periodic law.

After remarking on the evils arising from the system of competitive examinations, and after deploring the action taken by the London University in making chemistry an optional subject at the Matriculation examination—by certain of the licensing bodies of the medical profession in allowing preliminary training in natural science to be obtained elsewhere than in a college or school with recognised facilities—and by the military authorities in handicapping the study of physical science, the President then proceeded to direct attention to the possible existence of bodies which are not elements in the strictest sense of the word—bodies which he terms meta-elements.

No one doubts that oxygen, chlorine, sulphur and sodium are elements; even cobalt and nickel, near as they are to each other, are not denied separate elemental rank—although had solutions of their compounds presented identical colours it may be doubted whether their distinct nature would even now have been recognised. But on passing to the rare earths, the difficulty of arriving at a decision is very great, as in the case of Neodymium and Praseodymium, between which there may be said to be no well marked chemical difference—their chief claim to separate individuality being slight differences in basicity and crystallising power—though their physical distinctions as shown by spectrum observations are very marked. The majority of chemists probably would admit these two bodies within the charmed circle: but whether in so doing they would be able to appeal to any broad principle is an open question; and having once admitted them, how in justice can the elemental bodies or meta-elements made known by Krüss and Nilson—which exhibit well marked spectral differences—be excluded? In the same category are to be included the numerous separate bodies into which yttrium,

erbium, samarium and other "elements" commonly so-called have been, and are being split up. What then is the criterion of an element? Where shall the line be drawn? What is to be said when the only chemical difference is an almost imperceptible tendency of the one member of a couple or group to precipitate before the other; or when the chemical differences reach the vanishing point, though well-marked physical differences still remain? Is there no way out of the difficulty—must the elementary examination either be made so stiff that only some 60 or 70 candidates can pass, or must the examination doors be opened so wide that the number of admissions is limited only by the number of applicants? The real difficulty encountered by any unlimited multiplication of elements arises from the periodic theory, a theory which is so abundantly verified that we cannot lightly accept any interpretation of phenomena which fails to be in accordance with it. But if the usual conception of an element be modified, and for element we read "elementary group," such elementary groups being put into the places of the old elements in the periodic scheme, the difficulty is no longer felt. Let it be said, for example, that the smallest ponderable quantity of yttrium is an assemblage of ultimate atoms almost infinitely more like each other than they are to the atoms of any approximating element, but not all absolutely alike among themselves; that the atomic weight which we ascribe to yttrium, in fact, represents a mean value around which the weights of the individual atoms of the "element" range within certain limits. If this conjecture be tenable, could we separate atom from atom, we should find them varying within very narrow limits on each side of the mean. The very process of fractionation implies the existence of such differences in certain bodies.

Mr. Crookes then proceeded to discuss at length the meaning of the phenomena presented on fractionation, and also the processes of elemental evolution. Then, after quoting various statements of Clerk-Maxwell relating to our conceptions of molecules, among others, the passage—"Our molecules are unalterable by any of the processes which go on in the present state of things, and every individual of each species is of exactly the same magnitude, as though they had all been cast in the same mould like bullets, and not merely selected and grouped according to their size, like small shot," he went on to say:—"I think it evident that the statements referred to, some of which involve no small amount of assumption, no longer accord with facts, for we actually do find variations between the properties of certain molecules which heretofore had been pronounced identical with each other. Take the case of yttrium. It has its definite atomic weight; it behaves in every respect as a simple body, an element, to which we

may indeed add, but from which we can not take away. Yet this yttrium, this supposed homogeneous whole, on being submitted to a certain process of fractionation is resolved into portions not absolutely identical among themselves, and exhibiting a gradation of properties. Or taking the case of didymium: here was a body betraying all the recognised characters of an element. It had been separated with much difficulty from other bodies which approximated closely to it in their properties, and during this crucial process it had undergone very severe treatment and very close scrutiny. In short, until lately we might have said of it just what Clerk-Maxwell says of hydrogen, that the equality which we assert to exist between the molecules of didymium applies to each individual molecule, and not merely to the average of groups of millions of molecules. But then came another chemist, who, treating this assumed homogeneous body by a peculiar process of fractionation, resolved it into the two bodies praseodymium and neodymium, between which certain distinctions are perceptible. Further, we even now have no certainty that neodymium and praseodymium are simple bodies. On the contrary, they likewise exhibit symptoms of splitting up. Now if one supposed element on proper treatment is thus found to comprise dissimilar molecules, we are surely warranted in asking whether similar results might not be obtained in other elements, perhaps in all elements, if treated in the right way? We may even ask where the process of sorting-out is to stop? a process which of course presupposes variations between the individual molecules of each species. And in these successive separations we naturally find bodies approaching more and more closely to each other. Dr. Auer von Welsbach, the discoverer of neodymium and praseodymium, remarks that these bodies "approximate more closely to each other than any two supposed simple bodies yet known." Thus we approach nearer and nearer either to a regular gradation in the molecules or to the recognition of those intermediate links, which I have named "meta-elements." The conditions of elementary evolution were then discussed with reference to a periodic scheme modified from that of Prof. Emerson Reynolds, and the President then terminated his address thus:—"In this fashion, gentlemen, it seems to me that the great question of the elements may be provisionally treated. Our slender knowledge of these first mysteries is extending steadily, surely, though slowly. Whilst certain ardent chemists are testing the commonly received view of the homogeneity of the elements by methods of fractionation, others, by means of the spectroscope, are carrying on another form of assault; each worker bent on the one idea of undermining the secret. I earnestly recommend such researches. However successfully pursued, they cannot, I know, lead directly to any results capable of being turned to industrial account.

If, however, we consider the small but firm foothold we have gained in pursuit of this line of investigation, I venture to think there is reasonable ground to hope that these researches may tend to place chemistry upon a new foundation, by penetrating down through loose, superficial matter to the solid rock."

"The application of the luminous principle of evolution has remodelled and vivified many branches of biology; and philosophers are eagerly invoking its aid in other departments of science; I would fain hope that I may not be deemed unduly sanguine in believing that the application of this regenerating principle to chemistry will produce far-reaching effects on its harmonious and progressive development."

Dr. Gladstone then moved that thanks be given to the President for his address, and that he be requested to allow it to be printed. The motion was seconded by Dr. Atkinson, and carried with acclamation. The President having replied, the Treasurer, Dr. Russell, gave an account of the financial condition of the Society. The receipts by admission fees and subscriptions had been £3158; by sale of Journal, £351 11*s.* 1*d.*; by dividends on invested capital, £317 12*s.* 9*d.*; the whole income being £3896 2*s.* 10*d.* The expenses on account of the Journal had been £2116 10*s.* 4*d.*; on account of the Abstracts of Proceedings, £140 15*s.* 5*d.*; on account of the Library, £365 7*s.* 10*d.*; the total expenditure being £3194 1*s.* 4*d.* £300 had been invested in Metropolitan Board of Works 3½ per cent. stock, and there was a balance in hand of £1672 19*s.* 3*d.*

Dr. Stevenson moved that the thanks of the Society be tendered to the Treasurer for his services during the past session; Mr. J. A. R. Newlands seconded the motion. Dr. Russell acknowledged the vote.

A vote of thanks to the auditors was proposed by Professor Ramsay, seconded by Mr. Friswell, and acknowledged by Professor Dunstan.

Mr. Heaton proposed a vote of thanks to the Officers and Council; the vote was seconded by Professor Dunstan, and acknowledged by Dr. Armstrong.

Professor Clowes moved that the thanks of the Society be tendered to the Editors, Abstractors, and Librarian for their important services during the year. Dr. Plimpton seconded the motion. Mr. Groves and Dr. Thorne replied.

Messrs. Heron and Jackson having been appointed scrutators, a ballot was taken, and as result the following were declared elected as Officers and Council for the ensuing session:—

President: W. Crookes, F.R.S.

Vice-Presidents who have filled the office of President: Sir F. A. Abel, C.B., D.C.L., F.R.S.: Warren de la Rue, D.C.L., F.R.S.; E. Frank-

land, D.C.L., F.R.S.; J. H. Gilbert, Ph.D., F.R.S.; J. H. Gladstone, Ph.D., F.R.S.; A. W. Hofmann, D.C.L., F.R.S.; H. Müller, Ph.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, Ph.D., F.R.S.; Sir Lyon Playfair, Ph.D., K.C.B., F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents: G. Carey Foster, F.R.S.; David Howard; J. W. Mallet, M.D., F.R.S.; H. McLeod, F.R.S.; Ludwig Mond; C. Schorlemmer, Ph.D., F.R.S.

Secretaries: H. E. Armstrong, Ph.D., F.R.S.; J. Millar Thomson, F.R.S.E.

Foreign Secretary: F. R. Japp, M.A., Ph.D., F.R.S.

Treasurer: W. J. Russell, Ph.D., F.R.S.

Ordinary Members of Council: Messrs. T. Carnelley, D.Sc.; A. H. Church; Frank Clowes, D.Sc.; Wyndham Dunstan; P. F. Frankland, Ph.D.; R. J. Friswell; Charles W. Heaton; E. Kinch; H. F. Morley, M.A.; R. T. Plimpton, Ph.D.; Thomas Purdie, B.Sc.; W. Ramsay, Ph.D.

April 5th, 1888. Mr. W. Crookes, F.R.S., President, in the Chair.

Messrs. Sidney Skinner, Arthur W. Clayden and T. A. Elwood were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. John Campbell Fell, 15, Granby Street, N.W.; Albert Harrison, 66, Osborne Road, Forest Gate, E.; Egbert Grant Hooper, 24, Bloomfield Terrace, Buckingham Palace Road, S.W.; John Hughes, 3, West Street, Finsbury Circus; Henry James Kirkman, London Alkali Works, Swansea; William Parsons, 5, Earlsmead Road, South Tottenham, N.; Henry Charles Reynolds, 8, The Avenue, Clifton, Bristol; Frank Goodell Wait, University of Toronto, Canada.

The following Papers were read:—

27. "Researches on the Constitution of Azo- and Diazo-derivatives. III. Compounds of the Naphthalene β-series." By R. Meldola, F.R.S., and F. J. East.

The authors describe the action of nitrous acid on the azo-compounds produced from the diazotised nitranilines and β-naphthylamine. The products vary according to the mode of operating: if the nitroazo-compound be dissolved in a large quantity of acetic acid and sodium nitrite be added to the cold solution, a diazo-compound is formed, which decomposes normally on boiling the solution, thus:—

$NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}N_2{\cdot}OH = NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH + N_2$. If less acetic acid be used and the temperature be not allowed to exceed 60—70° at any stage of the operation, the change is of a different character, the acetic acid itself taking part: $NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}NH_2 + 2C_2H_3O{\cdot}OH + NaNO_2 = NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OC_2H_3O + N_2 + C_2H_3O{\cdot}ONa$. The details of the methods are given in the paper. The authors propose to make a special study of this last interaction, which promises to be of general application as a means of displacing NH_2 by $-O{\cdot}C_2H_3O$. Metanitrobenzenazo-β-naphthyl acetate melts at 161—162°, and the corresponding paranitro-compound at 192—193°.

The authors have also found that the acetyl-derivatives of the azo-β-naphthol compounds can be obtained by direct acetylation by long boiling with acetic anhydride and anhydrous sodium acetate. Metanitrobenzeneazo-β-naphthyl acetate thus prepared is identical with that obtained from the corresponding β-naphthylamine-compound by means of the diazo-compound and acetic acid in the manner described. Benzeneazo-β-naphthyl acetate prepared by the acetylation of benzeneazo-β-naphthol forms orange scales melting at 117°. A detailed examination of the products of complete reduction of the acetyl- and alkyl-derivatives is in progress. The authors refrain from expressing any view as to the constitution of the naphthalene β-azo-compounds till more experimental evidence has been obtained; but point out in conclusion that the present evidence indicates distinctly the presence of hydroxyl and amidogen in the β-oxyazo- and β-amido-azo-compounds of naphthalene respectively.

28. "The Action of finely divided metals on solutions of ferric salts, and a rapid method for the titration of the latter." By D. J. Carnegie, B.A.

Ferric salts, whether in aqueous or acid solution, are very rapidly, indeed almost instantaneously, reduced to ferrous salts by shaking with zinc-dust. The author describes a simple, very accurate, and very expeditious modification of the method for determining ferric salts by titration with permanganate, founded on this observation. The author considers that the zinc directly reduces the ferric salt, $Fe_2Cl_6Aq + Zn = ZnCl_2Aq + Fe_2Cl_4Aq$. If acid is not present some of the iron is precipitated partly as ferrous and partly as ferric hydroxide.

Many other finely divided metals, besides zinc-dust, effect the reduction of ferric chloride; in every case examined the heat of formation of the chloride of the metal is greater than the negative value of the thermal change accompanying the passage from Fe_2Cl_6 to Fe_2Cl_4.

Discussion.

Professor Ramsay remarked that he had for some years past employed zinc-dust instead of granulated zinc or zinc-foil to effect the reduction of ferric salts. When ferric salts are reduced by stannous chloride, the excess of reducing agent can readily be removed by the addition of mercuric chloride to the solution previous to titration with bichromate.

Mr. Carnegie stated that the use of powdered zinc had been suggested some years ago by Brown; the reduction, however, took place in the presence of acid, and was not a direct dechlorinating process such as that referred to in the paper.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

The Increase in the Produce of the Soil through the Rational Use of Nitrogenous Manures, by P. Wagner. Translated by G. G. Henderson. London 1888. From the Translator.

A Manual of the Geology of India. Part IV, Mineralogy, by F. R. Mallet. Calcutta and London 1887. From the Author.

Collection des Anciens Alchimistes Grecs, par M. Berthelot. Paris 1887. From the Author.

Ueber Paranitroso-diphenylamine, von M. Ikuta. Erlangen 1888. (*Pamphlet.*) From the Author.

Sixth Annual Report of the Board of Control of the New York Agricultural Experimental Station; for the year 1887. New York 1888. From the Board.

II. *By Purchase.*

Die Technologie der Fette und Oele des Pflanzen und Thier-reichs, von C. Schaedler. Leipzig 1883.

Die Thiophengruppe, von Victor Meyer. Braunschweig 1888.

Kurzes Handbuch der Kohlenhydrate, von B. Tollens. Breslau 1888.

Die Mikrophotographie, von P. Jesserich. Berlin 1888.

Des emplois chimiques du bois dans les Arts et l'Industrie, par O. Petit. Paris 1888.

A Treatise on Earthy and other Minerals and Mining, by D. C. Davis. London 1888.

Practical Treatise on Animal and Vegetable Fats and Oils, by W. T. Brannt. Philadelphia and London 1888.

Experimental Researches in Chemistry and Physics, by M. Faraday. London 1859.

A Course of Six Lectures on the Chemical History of a Candle, by M. Faraday. Edited by W. Crookes. London 1861.

The Subject-Matter of a Course of Six Lectures on the Non-metallic Elements, by M. Faraday; arranged by J. Scoffern. London 1853.

On the Various Forces of Nature and their Relation to each other, by M. Faraday. Edited by W. Crookes, London.

Aluminium, its History, Occurrence, Properties, Metallurgy, and Applications, including its alloys, by J. W. Richards. London 1887.

NOTICE TO AUTHORS OF PAPERS.

To facilitate the preparation of the abstract accounts of the Proceedings at the meetings of the Society, all authors are requested to furnish abstracts of their communications, and to send their papers so that they may be in the hands of the Secretaries, if possible, on the Monday before the day of meeting. Authors are also requested to write on their papers *the address to which they wish proofs to be sent.*

At the next meeting on April 19th, the following paper will be read:—

"The influence of temperature on the composition and solubility of hydrated calcium sulphate and of calcium hydroxide." By W. A. Shenstone and J. Tudor Cundall.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 52. Session 1888–89.

April 19th, 1888. Mr. W. Crookes, F.R.S., President, in the Chair.

Mr. James H. Gardner was formally admitted a Fellow of the Society.

A certificate was read in favour of Mr. George Thomas Evans, The Terrace, Rhymney, Mon.

The following were elected Fellows of the Society:—Ludwig Claisen, Ph.D.; Joseph Cowper; William Henry Dodd; John Gill; Frederick Preston de Jong; Thomas Enracht Lindsay, B.A.; Henry John Palmer; Eugene MacSwineef; John George Taylor; John Cecil Watson; Thomas Howell Williams; James Woodward.

The following Papers were read:—

29. "The Influence of temperature on the composition and solubility of Hydrated Calcium Sulphate and of Calcium Hydroxide." By W. A. Shenstone and J. Tudor Cundall.

The authors have with great care re-examined the effect of heat on hydrated calcium sulphate. They have experimented on specimens of natural as well as on others of artificial origin, and they find, contrary to the usual statements on the subject, that hydrated calcium sulphate parts with a portion of its water at moderate temperatures, *e.g.*, 40° C., and that it may be almost completely dehydrated in dry air at temperatures below 100° C. Thus a specimen of selenite heated at 70° C. for 36 hours lost 20·14 per cent. of water. The effect of heat in diminishing the solubility of calcium sulphate in water at temperatures between 40° C. and 150° C. may therefore possibly be due to the unequal solubility of the hydrated and anhydrous salts.

It is pointed out that the divergent statements made on this subject by various experimenters may be ascribed to the facts:— (1.) That at temperatures below 100° C. the dissociation of hydrated calcium sulphate proceeds at first very slowly, so that in an experiment continued for a short period only the effect of heat may very easily be overlooked; and (2) that specimens of hydrated calcium sulphate of diverse origin do not always behave in the same manner under identical treatment.

The authors have not yet found any evidence of the dissociation of calcium hydroxide at moderate temperatures, even by means of extremely delicate and very prolonged experiments. This has led them to re-examine the influence of heat on the solubility of this compound, because previous experiments have, so far as they are aware, been made in glass vessels, which, as recent experiments have shown, may have been attacked. They find that when a saturated solution of calcium hydroxide is heated at 150° C. in a platinum tube for some hours, the resulting solution contains only 1 part of hydroxide in 3081 parts of water. There is therefore no doubt that this substance is less soluble in hot water than in cold. But there seems to be no evidence at present in favour of the view that in this case diminished solubility also may depend upon the dissociation of the hydroxide, or of some hydrate of the hydroxide.

30. "Thermochemical Constants." By S. U. Pickering.

Heats of neutralisation, the differences between the heat of formation of similar salts of different metals, and the amounts of heat evolved on the introduction of the same radicle into various members of homologous series are often expressed by constant values, the meaning of which may be easily understood; but Thomsen (*Thermochem.*, 2) has also drawn attention to the fact that in many cases the heats of formation of analogous compounds, or the differences between their heats of formation, are multiples of constants. Thus:—

$$P_2,O_5 = 5 \times 73{,}980,$$
$$As_2,O_5 = 3 \times 73{,}130,$$
$$As_2,O_3 = 2 \times 77{,}330.$$

The existence of such a relationship, the author contends, can have no possible meaning, and he accounts for the occurrence of such coincidences as being simple mathematical chances. Given a certain number of quantities, it is easy to calculate the chances against any two of these being multiples of some constant, allowing a certain latitude for error, which allowance, it may be mentioned, attains considerable dimensions in many of the cases quoted by Thomsen.

Taking each case where an analysis of this description is possible, it is shown that there is a sufficient number of data to supply the coincidences observed by Thomsen.

He also criticises Thomsen's supposition as to the existence of a "common constant of affinity," a quantity the multiples of which by numbers up to 10 are supposed to represent various interactions, some of which are similar and others totally dissimilar (*Ber.*, **5**, 170; **6**, 239). This constant Thomsen takes as being 18,631 cal.; but the author contends that any other number taken at random would have given similar results. Taking, for instance, 15,000 cal., he finds that, out of the data quoted in Thomsen's second and third volumes, as many as 120 quantities are multiples of this number within the limits of error allowed by Thomsen; and out of these we may select a large number which represent actions just as analogous as many of those quoted by Thomsen. For instance—

$P,Cl_5 = 7 \times 14{,}998,$
$PCl_3,Cl_2 = 2 \times 14{,}845,$
$Ag,Cl = 2 \times 14{,}690,$
$K,Cl = 7 \times 15{,}087,$
$Mg,Cl_2 = 10 \times 15{,}101.$
$K,Br,Ag = 6 \times 15{,}038,$
$Zn,Br,Ag = 6 \times 15{,}160,$
$Sr,S,Ag = 7 \times 15{,}241.$
$Ca,I_2,Ag = 9 \times 14.993.$

31. "The action of hot Copper on the mixed vapours of Phenol and Carbon Disulphide." By Prof. Carnelley and John Dunn, University College, Dundee.

When a mixture of phenol and carbon disulphide is passed over hot copper a new diphenylene ketone, melting at 83°, is obtained isomeric with the diortho-ketone melting at 84°, already known, the interaction being—

$$2C_6H_5\cdot OH + CS_2 + 4Cu = 2Cu_2S + H_2O + C_6H_5\cdot CO\cdot C_6H_5$$
$$= 2Cu_2S + H_2O + H_2 + \begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix}\!>\!CO.$$

Even under favourable circumstances the yield only amounts to about 1 per cent. of the total mixture employed, as by far the greater portion (about six-sevenths) of the phenol passes over unchanged.

32. "Oxidation of Oxalic Acid by Potassium Dichromate." By Emil A. Werner.

In this paper the author gives the results of an exhaustive study of

the interactions of potassium dichromate and oxalic acid under different conditions and in varying molecular proportions. The results obtained are different from those described by Mr. Bothamley in a recent communication on the above subject (*Chem. Soc. Trans.*, 1888, 159), and may be summed up in the following conclusions:—

1. The red potassium dichromoxalate, $K_2H_2C_2(C_2O_4)_4(OH)_2$ (Croft's salt), is in all cases, *without exception*, a product of the interaction of potassium dichromate and hydrated oxalic acid below 200° C.

2. Neutral potassium chromate is *never* present as a product of the interaction of potassium dichromate and oxalic acid under any conditions below 200° C.

3. When the two compounds interact in the solid state, the initial emperature of the interaction, which lies between 30° and 60°, varies with the molecular proportions employed.

4. The dehydration of the oxalic acid does not affect the nature of the interaction, the anhydrous chromoxalate, $K_2Cr_2(C_2O_4)_4$, being formed in this case.

5. Water, by its solvent action, facilitates the interaction, *i.e.*, reduces the initial temperature, but is otherwise without influence on the nature of the change.

6. Seven molecules of oxalic acid is the *minimum* quantity necessary for the complete reduction of 1 mol. of potassium dichromate, and *any excess of either above this ratio remains unchanged.*

7. When the proportion of potassium dichromate to oxalic acid exceeds 1 mol. to 7 mols., and the temperature of the mixture is raised to low redness, a secondary interaction occurs between the excess of dichromate and the red chromoxalate first formed.

33. "The Action of Phenylhydrazine on Urea and some of its Derivatives." By Sidney Skinner, B.A., and S. Ruhemann, Ph.D.

The authors give an account of the action of phenylhydrazine on certain compounds nearly related to urea, describing several substances which complete the series of semicarbazides and carbazides both of oxy- and thio-urea, *e.g.*, diphenylcarbazide, $CO(NH{\cdot}NH{\cdot}Ph)_2$, from phenylhydrazine and ethylic carbamate or urea; and diphenylsemicarbazide, $Ph{\cdot}HN{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}Ph$, from phenylurea and phenylhydrazine. The compounds which contain two directly-linked nitrogen-atoms are found to exhibit a characteristic behaviour with mild oxidising agents —cupric sulphate and mercuric chloride—yielding coloured compounds; and in this respect they differ in a marked manner from urea. Biuret and phenylhydrazine interact to form ammonia and Pinner's phenylurazole. In the latter part of the paper, the action of phenylhydrazine on parabanic acid and on alloxan is considered.

34. "Derivatives of Phenylisobutyric Acid." By L. Edeleanu, Ph.D.

The derivatives described are paranitrophenylisobutyric acid, m. p. 121°; orthonitrophenylisobutyric acid, an oil; parorthodinitrophenylisobutyric acid, m. p. 89°, and its methylic salt, m. p. 76°; nitroamidophenylisobutyric acid, m. p. 138°; amidomethylhydrocarbostyril, m. p. 216°; the last-mentioned being obtained by complete reduction of the dinitro-acid.

35. "The Logarithmic Law of Atomic Weights." By G. Johnstone Stoney, F.R.S.

A verbal explanation was given of a paper on this subject, which the author had that day read at the Royal Society.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Chemical Essays, by R. Watson. 5 vols. 12mo. London 1787.
From Dr. T. Stevenson.

A Treatise on Alcohol with Tables of Spirit Gravities, by T. Stevenson, London 1888. From Dr. T. Stevenson.

Ausführliches Lehrbuch der Chemie, von H. E. Roscoe and C. Schorlemmer. Vierter Band: die Kohlenwasserstoff und ihre Derivate, oder Organische Chemie: zweiter Theil, dritte Abtheilung. Zweite Auflage, zweite Band, erste Abtheilung.
From Sir Henry E. Roscoe, F.R.S.

NOTICE TO AUTHORS OF PAPERS.

To facilitate the preparation of the abstract accounts of the Proceedings at the meetings of the Society, all authors are requested to furnish abstracts of their communications, and to send their papers so that they may be in the hands of the Secretaries, if possible, on the Monday before the day of meeting. Authors are also requested to write on their papers *the address to which they wish proofs to be sent.*

The following lectures will be given on Wednesday afternoons, at 4 P.M., under the auspices of the College of State Medicine; Fellows of the Chemical Society who may be interested in the lectures are invited to attend.

May 2. "The Aims and Objects of State Medicine." By R. Brudenell Carter, F.R.C.S.

May 16. "Soil in its Influence on Health." By Professor H. G. Seeley, F.R.S.

May 30. "The Organisms occurring in Fresh Water, and the Hygienic Importance of their Presence." By Inspector-General John M. Macdonald, M.D., F.R.S.

June 13. "Some of the more Important Diseases Common to Man and Animals." By G. Fleming, Esq., LL.D., C.B., &c.

June 27. "The Rise and Progress of Sanitary Engineering within the Present Century." By Sir Robert Rawlinson, K.C.B.

July 11. "Responsibility and Disease." Sir J. Crichton Browne, M.D., LL.D.

At the next meeting on May 3rd, the following paper will be read:—

"The Determination of the Molecular Weights of the Carbohydrates." By Horace T. Brown and G. H. Morris, Ph.D.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 53. Session 1888–89.

May 3rd, 1888. Mr. W. Crookes, F.R.S., President, in the Chair.

Certificates were read in favour of Messrs. Joseph Campbell, Glen Innes, New South Wales; John Dunn, Myrtle Cottage, Downfield, Dundee; William Burns Featherstone, Showelhurst, Moseley, Birmingham; Albert L. Guiterman, Ph.D., 36, Primrose Hill Road; James C. Hamilton, King's Cavil, Linlithgow, N.B.; James Mair, B.Sc., 181, Hospital Street, Glasgow, S.S.; Edward William Alfred Augustine Mayhew, Freemantle, Western Australia; John James Morgan, Highfield House, Ebbw Vale, Monmouth; Frederick Ernest Pollard, Administration des Services Sanitaires et d'Hygiène Publique, Cairo, Egypt; Albert John Sach, Goulburn, New South Wales, Australia; Mark S. Wade, M.B., Clinton, British Columbia.

The following papers were read:—

36. "The Determination of the Molecular Weights of the Carbohydrates." By Horace T. Brown and G. Harris Morris, Ph.D.

The molecular weights of the carbohydrates have, with one or two exceptions, never been determined with any certainty. The exceptions—dextrose and levulose—have been shown indirectly by Kiliani to have a molecular weight corresponding to the formula $C_6H_{12}O_6$. The generally accepted views with regard to the other carbohydrates are based entirely upon certain indefinite derivatives, and only give the *minimum* size of the molecules. Quite recently V. Meyer (*Ber.*, 1888, 556) and Auwers (*ibid.*, 1888, 860) have drawn attention to the method devised by Raoult for the determination of molecular weights. The method is applicable to all organic substances, and is of especial value in ases where a vapour-density determination is not possible. Blagden, in 1788, established the fact with regard to inorganic salts that the lowering of the freezing point of their aqueous solutions is proportional to the weight of substance dissolved in a constant weight

of water. De Coppet in 1871–72 extended these results and pointed out that when the lowering of the freezing point is calculated for a given weight of the substance in 100 grams of water, the result, which he terms the *coefficient of depression*, is constant for the same substance, and that the coefficients for different substances bear a simple relation to their molecular weights.

Raoult extended the law to organic substances and to other solvents besides water. He showed that when certain quantities of the same substance are successively dissolved in a solvent upon which it has no chemical action, there is a progressive lowering of the point of congelation of the solution, and this lowering is *proportional to the weight of the substance dissolved in a constant weight of water.* If C be the observed depression of the point of congelation produced by x grams of the substance dissolved in y grams of the solvent, then the depression A produced by 1 gram of the substance in 100 grams of the solvent is given by the formula $\frac{C \times y}{x \times 100} = A$. If the value A, which Raoult designates the "coefficient of depression," of the respective substance for the respective solvent is multiplied by the molecular weight M of the dissolved substance, we get $M \times A = T$, the so-called "molecular depression" of the substance in question. T is a value varying with the nature of the solvent, but remaining constant with the same solvent for numerous groups of compounds. Raoult finds that for water T = 19 for all organic substances with one or two exceptions. From this it follows that having determined experimentally the value of A for any substance, and knowing the value of T, the molecular weight M for the substance in question may be obtained by dividing A into T: for $M = \frac{T}{A}$.

The method employed by the authors is essentially that of Auwers (*Ber.*, 1888, 712), the solvent employed being necessarily water. The thermometer used is graduated into twentieths of a degree centigrade, and with the aid of a telescope can be easily read to one two-hundredth of a degree. The following results were obtained:—

Dextrose.—Calculated for $C_6H_{12}O_6$.	Found (mean).
A = 0·106	A = 0·1052
M = 180·0	M = 180·2

Cane-sugar.—Calculated for $C_{12}H_{22}O_{11}$.	Found (mean).
A = 0·0555	A = 0·0562
M = 342·0	M = 337·5

Maltose.—Calculated for $C_{12}H_{22}O_{11}$.	Found (mean).
A = 0·0555	A = 0·059
M = 342·0	M = 322·0

Milk-sugar.—Calculated for $C_{12}H_{22}O_{11}$.	Found (mean).
A = 0·0555	A = 0·055
M = 342·0	M = 345·0

A solution of cane-sugar inverted with *invertase* gave before inversion M = 328, after inversion M = 174·3: clearly showing that 1 mol. of cane-sugar splits up on inversion into two equal molecules.

It was found that dextrose which exhibits birotation in solution has the same molecular weight as dextrose having the normal rotation.

Mannitol.—Calculated for $C_6H_{14}O_6$.	Found (mean).
A = 0·104	A = 0·105
M = 182·0	M = 181·0

Arabinose.—Calculated for $C_5H_{10}O_5$.	Found (mean).
A = 0·126	A = 0·1263
M = 150·0	M = 150·3

Raffinose.—Calculated for $C_{18}H_{32}O_{16}·5H_2O$.	Found (mean).
A = 0·032	A = 0·036
M = 594·0	M = 528·0

All the results are the mean of numerous extremely concordant experiments made with solutions of varying concentration.

All the saccharoses—cane-sugar, maltose and milk-sugar—were found to have the same molecular weight, thus disproving the suggestions of Herzfeld and others as to their varying values.

The authors have applied the method to *starch* and the non-crystallisable products of its transformation, but owing to unexpected difficulties, resulting from the smallness of the value of A for these substances, they are unable as yet to assign accurate values to them, although there can be no doubt that their molecular weights are extremely high.

37. "The Molecular Weights of Nitric Peroxide and Nitrous Anhydride." By W. Ramsay, Ph.D.

The author has applied Raoult's method of determining molecular weights to nitric peroxide, and has ascertained the depression produced in the freezing point of pure glacial acetic acid by quantities of peroxide varying from 0·92 gram to nearly 9 grams of peroxide to 100 grams of acetic acid. It is found that in every case the molecular weight of the peroxide is nearly 92, corresponding to the formula N_2O_4; the highest result was 98·58 and the lowest 90·29. These experiments establish the molecular weight of liquid nitrogen peroxide, even in dilute solution, and also show that no further molecular aggregation occurs even when the number of molecules of peroxide in a given volume is considerably increased.

Similar experiments were made with nitrous anhydride, but the temperature of experiment (about 16°) is so high that dissociation occurred during manipulation. No definite results were obtained.

Discussion.

Professor Debus said he presumed that on dissolving urea in acetic acid combination would occur. Would the molecular weight found be the same if a neutral solvent were used? Also, did not acetic acid act on nitrogen tetroxide? Most liquids exerted a decomposing action on this substance. He was under the impression that Raoult's method involved the use of a solvent which had no chemical action on the substance.

Mr. Wynne remarked that the molecular weight of acetic acid determined by Raoult's method accorded with the formula $C_2H_4O_2$. Now it was known that the vapour-density of acetic acid at a few degrees above its boiling point pointed to the formula $C_4H_8O_4$, and that it was only at higher temperatures that the less complex molecule $C_2H_4O_2$ was obtained. It must, therefore, be assumed that the action of the solvent resulted in the complete dissociation of the complex molecules present in liquid acetic acid. Most results hitherto obtained by the use of Raoult's method pointed to a similar complete dissociation and would seem to show that the dissociation is not dependent on the particular solvent employed but took place in all cases; the method, therefore, had so far failed to afford any indication of the molecular complexity of liquids and solids.

Referring to the formula $C_{12}H_{22}O_{11}$ deduced by Messrs. Brown and Morris by Raoult's method, Mr. Wynne asked what interpretation was to be placed on the results recently obtained by Winter in his investigation of the specific rotatory power of levulose and of invert sugar, which pointed to the presence in the latter of 3 mols. levulose and 4 mols. dextrose. If these results were accepted it would seem reasonable to suppose that the complexity of the molecule of cane-sugar was greater than that indicated by the formula quoted.

Dr. Perkin said that he had obtained results confirmatory of those brought forward. Using acetic acid as solvent, the molecular weight of naphthalene was found to be 134, and the values he had obtained for the isomeric citraconic, itaconic, and mesaconic acids were respectively 130·6, 130·9 and 138, the calculated value for the simple formula $C_5H_6O_4$ being 130.

Mr. Crompton observed that great irregularities were manifest on comparing the molecular depressions of various substances as determined by Raoult: therefore, until more was known of the cause of such irregularities and of the mechanism of the changes under

discussion, such results as those brought forward by Messrs. Brown and Morris must, he thought, be accepted with great reservation.

Dr. Armstrong said that the results obtained by Raoult's method were certainly very striking, but bearing in mind the complexity of the phenomena of dissolution, as there was undoubtedly much evidence to favour the conclusion that the molecules of many substances in the solid and even in the liquid state were congeries of the *fundamental* molecules, he was not prepared to accept the conclusions arrived at as in any way final. If Winter's results were accepted, it would be difficult to reconcile them with the conclusion that cane-sugar was represented by the simple formula $C_{12}H_{22}O_{11}$. Apart from the information as to the comparative molecular weights of dissolved substances which Raoult's method promised to afford, it appeared that in order to gain as complete insight as possible into the molecular composition of solids and liquids it was important to vary in every way the proportions of substance dissolved as well as the solvent: he therefore regarded V. Meyer and Auwers' recent recommendation of acetic acid as *the* solvent as most unfortunate.

Mr. Heron doubted the correctness of Herzfeld and Winter's determinations of the rotatory power of levulose.

Mr. Brown agreed with Mr. Heron that Winter's statement regarding levulose required confirmation. The values obtained by Raoult were remarkably uniform for members of a group of compounds, and he was of opinion that the general consistency of the results obtained in the case of organic compounds was such as entirely to justify the claim that the results put forward by Mr. Morris and himself were to be accepted as expressing the facts.

Professor Ramsay asked: Was urea acetate known? [Beilstein does not mention it, although he describes the trichloracetate. Gmelin says that the lactate cannot exist, and states that urea does not combine with weak acids. Moreover, its formation would not materially affect the result, as it would only be equivalent to the withdrawal of a small portion of the acid.] N_2O_4 was without action on acetic acid; it, however, served as a most delicate test of water, a green colour being produced if water were present in the acid. He agreed that as great a variety of solvents as possible should be used.

38. "The Action of Heat on the Salts of Tetramethylammonium." By A. Th. Lawson, Ph.D., and Norman Collie, Ph.D.

The research was undertaken to ascertain how the tetramethylammonium salts would behave when heated and in what respects they would resemble the phosphonium and sulphine compounds. Most of the salts experimented with were found to be very deliquescent and far more soluble than the corresponding ammonium salts,

and when compared with the ammonium salts the order of solubility seemed in some cases to be reversed: in the case of the halogen salts the iodide is least soluble, the chloride and fluoride the most soluble. The oxalate and sulphate are extremely deliquescent, while the nitrate is one of the least soluble of the tetramethylammonium compounds and scarcely deliquescent. Nearly all the salts experimented on split up in a simple manner, trimethylamine and a salt of methyl being produced. The fluoride is an instance: $(CH_3)_4NF = (CH_3)_3N + CH_3F$. But in some cases where the decomposition takes place at a high temperature and the methyl salt which is formed is not very stable, further decomposition occurs; of this kind of decomposition the nitrite is an example:—$4(CH_3)_4N{\cdot}NO_2 = 4(CH_3)_3N + 2(CH_3)_2O + 4NO + O_2$.

39. "The Action of Heat on the Salts of Tetramethylphosphonium." By Norman Collie, Ph.D., F.R.S.E.

The action of heat on the salts of tetramethylphosphonium was studied, partly to complete a series of experiments which had been made on the mode of decomposition of the phosphonium salts when heated and partly to compare their decomposition with that of the tetramethylammonium salts when similarly treated.

The salts of tetramethylphosphonium with the oxy-acids, when subjected to the action of heat, undergo, as a rule, two different changes: the first and by far the most important is the production of trimethylphosphine oxide and a ketone—in the case of the benzoate: $(CH_3)_4PCO_2C_6H_5 = (CH_3)_3PO + CH_3{\cdot}CO{\cdot}C_6H_5$. The second change, and one which only occurs to a very limited extent, is when trimethylphosphine and a salt of methyl are produced: $(CH_3)_4PCO_2C_6H_5 = (CH_3)_3P + C_6H_3{\cdot}CO_2C_6H_5$.

As regards the action of heat on the hydracid salts, the chloride is the only one which decomposes in a simple manner: $2(CH_3)_4PCl = 2(CH_3)_3PHCl + C_2H_4$.

At the next meeting, on Thursday May the 17th, there will be a ballot for the election of Fellows, and the following paper will be read:—

"Researches on the Constitution of Azo- and Diazo-derivatives. IV. Diazo-amido Compounds." By Professor Meldola, F.R.S., and F. W. Streatfeild, F.I.C.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 54. Session 1888–89.

May 17th, 1888. Mr. W. Crookes, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. John Alexander, M.A., 14, Caledonia Place, Perth; Charles Bradshaw, 174, Nottingham Street, Sheffield; Lewis Edmunds, 8, Grafton Street, Piccadilly, W.; William Humphrey Gibson, 107, King's Road, Brighton; Joseph Henry Maiden, Sydney, New South Wales; Henry Alexander Miers, M.A., Eden Cottage, Beckenham, Kent; Frank Mousley, Phillimore Terrace, Walham Green, S.W.; James Henry Rymer Paterson, 10, Millerfield Place, Edinburgh; George Woodyatt Procter, 18, Alice Street, Sunderland; Herbert W. Seeley, 11, Corn Market, Halifax.

The following were elected Fellows of the Society:—George Thomas Evans, John Campbell Fell, Albert Harrison, John Burchmere Harrison, M.A., Egbert Grant Hooper, John Hughes, Henry James Kirkman, William Parsons, Henry Charles Reynolds, Frank Goodell Wait.

The following papers were read:—

40. "Researches on the Constitution of Azo- and Diazo-derivatives. IV. Diazo-amido-compounds." By Professor Meldola, F.R.S., and F. W. Streatfeild.

Expressing the constitution of the mixed diazo-amido-compounds by the general formula $X{\cdot}N_3H{\cdot}Y$, the authors point out that in former papers they had given evidence that the alkyl-derivative $X{\cdot}N_3R'{\cdot}Y$ was capable of existing in three isomeric modifications:—(1) from the action of $X{\cdot}N_2{\cdot}OH$ on $Y{\cdot}NH{\cdot}R'$; (2) from the action of $Y{\cdot}N_2{\cdot}OH$ on $X{\cdot}NHR'$; (3) from the direct alkylation of the compound produced by the action of $X{\cdot}N_2{\cdot}OH$ on $Y{\cdot}NH_2$, or of $Y{\cdot}N_2{\cdot}OH$ on $X{\cdot}NH_2$.

The only known case at present established is that of the ethyl-derivatives of para-meta-dinitrodiazoamidobenzene, and the object of the present investigation has been to obtain other series of isomeric triplets. The triplet of methyl-derivatives is first described. By the direct methylation of the mixed para-meta-compound a derivative of m. p. 148° is obtained. By the action of diazo-*p*-nitrobenzene chloride on methyl-*m*-nitraniline a derivative is obtained melting at 168°. The third isomeride, formed by the action of diazotised *m*-nitraniline on methyl-*p*-nitraniline, melts at 176—177°. The triplet is thus shown to confirm the isomerism indicated by the ethyl-derivatives. Methyl-derivatives of *p*-dinitrodiazoamidobenzene (m. p. 219°) and the corresponding *m*-compound (m. p. 127—128°) have also been prepared. A considerable number of other new diazoamido-compounds have been obtained in the course of a search for triplets of alkyl-derivatives, of which two members at least are required as solids. It has been found that mixed diazoamido-compounds cannot be obtained from the nitranilines and *p*-chloraniline, as the resulting product is always a mixture of the two symmetrical compounds. A very small quantity only of the mixed compound $(p)NO_2{\cdot}C_6H_4{\cdot}N_3H{\cdot}C_6H_4Cl(p)$ is formed under certain conditions by the action of diazotised *p*-nitraniline on *p*-chloraniline. In conclusion, the authors give a series of numerical results obtained by the analytical method described by them in a former paper, and which show that the amount of azonaphthol-compound, $X{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH\beta + Y{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH\beta$, produced by the decomposition of the diazoamido-compounds by hydrochloric acid represents the quantitative resolution :—$2X{\cdot}N_3H{\cdot}Y + 2HCl = X{\cdot}N_2{\cdot}Cl + X{\cdot}NH_2 + Y{\cdot}N_2{\cdot}Cl + Y{\cdot}NH_2$.

41. "The Colour of some Carbon Compounds." By Thomas Carnelley, D.Sc., and John Alexander, M.A., University College, Dundee.

A careful investigation of a number of metallic derivatives of ortho- and para-nitrophenol has given the following results :—(1) In all cases without exception the colour passes towards the red end of the spectrum as the temperature rises. Organic compounds thus behave like inorganic substances. (2) The colour of the ortho-derivative is nearer the red end than that of the corresponding para-compound. Para-compounds almost always melt higher than either of the corresponding ortho- or meta-compounds, and the probability is that of two isomeric bodies which are of different colour the one with the lower melting point will have a colour nearer the red end of the chromatic scale than the one with the higher melting point. This is only what we should *a priori* expect, for the compound with the lower melting

point is at a correspondingly higher temperature than the other, and according to (1) the higher the temperature the more does the colour pass towards the red end. (3) A comparison of the nitrophenates of metals belonging to the same sub-group shows that the colour passes towards the red end as the atomic weight of the metal increases. This accords with the results observed by one of the authors (*Phil. Mag.*, 1884 [5], **18**, 130) in the case of inorganic salts. (4) When the same salt occurs in both the anhydrous and hydrated state, the colour passes towards the red end as the quantity of water of crystallisation diminishes. The exceptional behaviour in this respect of such inorganic salts as copper sulphate is possibly due to the breaking down of the crystals on dehydration, which of itself frequently makes a coloured body become white or nearly so. (5) As regards the salts investigated, the para-compound always takes up a larger quantity of water of crystallisation than the corresponding ortho-compound.

Discussion.

Dr. Armstrong remarked that the facts advanced were far too few to justify the very general conclusions arrived at by the authors; all who had worked with the nitrophenols were well aware that the colour changed on heating in the manner described; and there was no novelty in the statement that the paranitrophenates crystallised with the larger proportion of water. Referring to the suggested explanation of the colourlessness of dehydrated copper sulphate, he quoted calcium parachlorodiorthonitrophenate as one of the exceptions to which such an explanation did not apply: this compound could be obtained either in yellow anhydrous crystals, or in deep-orange hydrated crystals.

Mr. Friswell mentioned magnesium and barium platinocyanide as instances of loss of colour taking place without loss of crystalline form; the hydrated magnesium compound was of a splendid red colour, but when gently heated it became lemon-yellow, and when anhydrous it was white; if care were taken, the dehydration could be effected without the slightest apparent injury to the crystals.

Professor Thorpe said that he and Professor Judd had recently had occasion to examine the cyanides referred to, and he thought that in reality the dehydrated crystals were mere pseudomorphs.

Mr. Warington mentioned having succeeded in expelling the ammonium sulphate from ammonium magnesium sulphate without changing the form of the crystals.

42. "The Identity of natural and artificial Salicylic Acid." By W. N. Hartley, F.R.S.

In order to determine whether natural and artificial salicylic acid

are the same substances, specimens prepared by Kolbe's process and from oil of winter-green were carefully recrystallised and examined by means of the spectrum. They were found to give identical series of photographs, and hence the same curve.

43. "Researches on the relation between the Molecular Structure of Carbon compounds and their Absorption-spectra. (Part VIII.)" By W. N. Hartley, F.R.S.

Isomeric Cresols, Dihydroxybenzenes and Hydroxybenzoic Acids.—The ultra-violet spectra of these substances were carefully examined, with the object of ascertaining how far they are alike or different from each other.

The *oscillation frequencies* of the extreme rays transmitted by 1 mgrm.-molecule of the four series of substances, including xylenes previously examined, are the following:—

	Xylenes.	Cresols.	Dihydroxy-benzenes.	Hydroxy-benzoic acids.
Ortho	3611	3433	3466	3359
Meta	3580	3413	3399	3080
Para	3537	3359	3151	2986

It appears from this table that the law which determines the order of greatest absorption is not the same in the series of isomeric hydrocarbons as in the series of cresols and dihydroxybenzenes. In the hydroxybenzoic acids it is the reverse of that in the xylenes.

The curves of molecular vibrations afford evidence of the relative extent to which energy is dissipated during the formation of the molecules of the substances, and they are classified according to the indications of the curves.

44. "A Definition of the term Atomic Weight and its reference to the Periodic Law." By W. N. Hartley, F.R.S.

The atomic weights are too frequently viewed by those who become familiar with them in the capacity of teachers or as students, either as proportional weights, as combining weights, or as mere numbers with which calculations can be made for analytical or other purposes. That they are real measures of the *quantity of matter* in the atoms of the elements is often overlooked. The reason of this is due to the ambiguous use of the word *weight*. A weight is a measure of the attraction between the earth and the matter weighed, or as it is more familiarly stated, a measure of the *earth's attraction* for the body

weighed. The common method of determining relative quantities of matter is by weighing, and though the determination of the weight of a body does not actually determine its mass, yet the weight of a substance is proportional to its mass.

A so-called atomic weight is therefore a numerical proportion. There are 70 elements and 70 atomic weights, and these represent 70 different quantities of matter in 70 different atoms; or in other words, they represent matter in 70 different states of condensation.

I am of opinion that the teaching of chemistry is very much facilitated by the use of the following definition, which I have used for some years past, and I would recommend its general adoption :—*The atomic weight of an element is the ratio of the mass of its atom to the mass of an atom of hydrogen.*

The term atomic weight should be abolished and atomic mass substituted. Similarly, molecular weight should be defined as the *mass of a molecule* or *molecular mass.* The statement that the molecular weight of a compound is the sum of the weights of the atoms of the elements contained in it becomes simplified thus :—*The mass of a molecule is the sum of the mass of its constituent parts.*

Whatever remarks are applicable to the inconveniences arising from the term atomic weight, they may be emphasised in dealing with the Periodic Law. If we accept it as correctly stated, thus :—The properties of the elements are a periodic function of their atomic weights; then the ambiguous use of the word weight, and the tendency to see in the atomic weights only a series of numbers, obscures the true meaning of the law. A quotation from a recently published paper of great interest affords evidence that an important corollary of the law has been overlooked. Thus Professor Roberts-Austen refers to the fact that " Carnelley has given strong evidence in favour of supplementing the law as follows :—" The properties of *compounds* of the elements are a periodic function of the atomic weights of their constituent elements.' " (*Proc. Roy. Soc.*, **43**, 425, 1888.) This was recognised by Mendelejeff, for he headed the columns in his table of the atomic weights with their most characteristic oxygen and hydrogen compounds, such as M_2O, MO, M_2O_3, $\frac{H_4M}{MO_2}$, $\frac{H_3M}{M_2O_5}$, &c. Furthermore, he predicted the properties of the various hydrates, oxides and salts of scandium with most remarkable accuracy when he described those of eka-boron. Inasmuch as the properties of compound substances depend almost entirely upon their composition, and that both the chemical and physical properties of the elements are a periodic function of their so-called atomic weights, it follows that the periodical relationship must influence the compounds into which the atoms enter. During the last six years I have made a

practice of stating the periodic law in a much more concise and at the same time comprehensive manner, thus:—*The properties of the atoms are a periodic function of their masses.*

Thus the chemical and physical properties of both elements and compounds are directly connected with the quantity of matter entering into them.

In any graphic representation of the periodic law the fact that it is upon the mass of the atoms that their properties depend should appear prominently. The diagram of Dr. G. Johnstone Stoney, F.R.S., used to illustrate his paper on the "Logarithmic Law of Chemistry," recently read before the Royal Society, has on this account alone a pre-eminent importance.

The elements are distributed on a logarithmic curve of the second order, their masses being represented by volumes which are proportional to radii by which the curve is described and which are derived from numbers which are the cube roots of the atomic weights. Its most essential feature is a representation of the ratios of the masses of the atoms of other elements to the mass of the atom of hydrogen, and the consequent variation in chemical and physical properties accords with the positions of the elements upon the diagram.

At the next meeting on June 7th there will be a ballot for the election of Fellows, and the following papers will be read:—

"The Chemical Action of some Micro-organisms." By R. Warington, F.R.S.

"The Optical and Chemical Properties of Caoutchouc." By J. H. Gladstone, F.R.S., and W. Hibbert.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 55. Session 1888–89.

June 7th, 1888. Mr. W. Crookes, F.R.S., President, in the Chair.

Professor Ferguson and Messrs. John Campbell Fell and Thomas E. Lindsey were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Walter Bromley Cooley, 5, Dudley Street, Wolverhampton; Archibald Carlyle Mounsey Ingram, 5, Buchanan Terrace, Paisley; Walter M. Gardner, Brookfield Terrace, Headingly, Leeds; Frank Pullinger, B.A., Alexander Park, Oldham; Clement T. Rhodes, 18, Bute Street, South Kensington.

The following were elected Fellows of the Society:—Messrs. Joseph Campbell, John Dunn, William Burns-Featherstone, Albert L. Guiterman, James C. Hamilton, James Mair, B.Sc., John James Morgan, Edward W. A. Augustine Mayhew, Frederick Ernest Pollard Albert John Sach, Mark S. Wade, M.D.

The following papers were read:—

45. "The Chemical action of some Micro-organisms." By R. Warington.

The organisms whose action has been studied were *B. subtilis;* two bacilli isolated from soil; one from a visible growth in a solution which had nitrified; a micrococcus isolated from another culture in which it was present as an impurity; 18 organisms, many pathogenic received from Dr. Klein, F.R.S., and one from Dr. W. R. Smith.

1. *The Hydrolysis of Urea.*—The ability of each organism to render a sterilised 25 per cent. solution of urine alkaline was tested. In every case but two there was either no increase of alkalinity in one week at 22°, or the increase was so slight that it could not be safely concluded that ammonia was produced. In the case of the *M. ureæ* isolated by

Dr. Smith, a rather considerable increase of alkalinity took place. A somewhat smaller but very distinct increase occurred with *B. fluorescens non liquescens*. A much larger increase of alkalinity than in either of these instances was obtained when the urine was seeded with a fragment of arable soil.

2. *Behaviour in Milk.*—The curdling of milk by micro-organisms is effected either by the production of lactic acid, or apparently by the formation of a rennet-like ferment. The amount of lactic acid required to curdle milk depends on the temperature, the amount being smaller the higher the temperature.

Among the organisms examined five have distinctly acidified milk, but in very different degrees. *Staphylococcus candidus* produces too little acid to cause curdling, even when the milk, after acidification, is placed in boiling water. The bacillus of infantile diarrhœa and *B. termo* produce a greater acidity, curdling milk speedily at 32°, but fail entirely to curdle it at 22°. *M. gelatinosus* curdles milk speedily at 22°, and even at 10° after many days. The two organisms, *B. fluorescens liquescens* and Koch's cholera spirillum curdle milk readily at 22°, without producing any appreciable acidity; the latter organism will indeed curdle milk made alkaline with sodium carbonate without destroying the alkalinity. We have here, apparently, a typical case of curdling by means of a ferment. Two of the acidifying organisms which curdle milk, *M. gelatinosus* and *M. ureæ*, act apparently in part by means of a ferment, as the acidity produced by them when the milk is curdled is quite insufficient in itself to effect curdling at the temperature of the experiment. Soil from an arable field readily curdles milk, even at 10°, but without producing at the time an appreciable acidity; it acts plainly by a ferment. During the action of soil on milk much gas is evolved, even at 10°. No gas was observed during the action of any of the organisms examined, save in an experiment with the bacillus of infantile diarrhœa at 37°.

Five organisms, *B. subtilis*, *B. anthracis*, *B. floccus*, *B. toruliformis*, and Finkler's comma are active peptonisers. The milk, after a few days at 22°, becomes clear immediately beneath the surface, and this clear space slowly extends till the whole of the milk has lost its opacity. On moving the tube after the action has begun, it is found that the opaque portion is more or less gelatinised. The clearing of the milk is due to the gradual dissolution of the jelly. The clear fluid is rich in peptone. It has been supposed that the liquefaction of gelatin by bacteria is due to the production of a ferment. The whole of the liquefying bacteria experimented on show evidence of the formation of ferments when grown in milk. The organisms which simply acidify do not liquefy. Soil peptonises

after curdling, the curd first formed slowly redissolving. A small class of organisms, *B. fluorescens non liquescens* and the bacillus of septicæmia (mouse and guinea pig), render milk after a time decidedly alkaline, and the milk from this cause loses much of its opacity, but no other change is produced. Several organisms grow freely in milk without altering its appearance or its reaction to litmus-paper. Cultivation in milk is an excellent method of distinguishing micro-organisms, the possible results being very varied, especially when the effect of temperature is observed.

3. *Reduction of Nitrates.*—Nearly the whole of the organisms examined have been cultivated both in broth containing nitre and in a 20 per cent. solution of urine containing nitre, and generally at two temperatures, 20—23° and 32—37°. The experiments were made in half-filled bottles with cotton-wool stoppers. The amount of nitrate reduced in urine was always small and varied probably on account of the variable composition of the medium. The reduction of nitrate in broth was frequently both rapid and very considerable. In cases in which the organisms would bear a high temperature the reduction was always more energetic at the higher than at the lower temperature. The organisms which appeared to possess the greatest power of reducing nitrates to nitrites were—

B. floccus, *B. fluorescens non liquescens*, B. of swine fever, *M. ureæ*, *M. gelatinosus*, *Staph. candidus*, *Staph. luteus*. Next to these stand the following, which also reduce nitrates freely:—*B. termo*, B. of typhoid fever, B. of infantile diarrhœa, B. of cholera, B. of septicæmia, *B. anthracis*, B. Denicke's comma, *Staph. albus liquescens*.

Far below these comes *B. subtilis*, which produces no nitrite in the urine solution, but always yields, after some time, a trace of nitrite in broth at the lower temperature, and a much more marked amount at the higher temperature. *Streppococcus scarlatinæ* yields a mere trace of nitrite in broth cultures.

The following organisms failed entirely to effect reduction to nitrites:—*B. fluorescens liquescens*, *B. toruliformis*, *B. sulphureus*. B. Finkler's comma, *B. comma noma*, *M. aureus*.

Most of the non-reducing organisms were also cultivated in broth containing nitre covered by a layer of paraffin oil, by which means the access of oxygen was to a considerable extent excluded. In no case was any reduction of nitrates observed.

No evolution of gas was noticed in any of the above cultivations. In experiments made in solutions seeded with arable soil, air being excluded, the reduction of nitrates was complete, gas being evolved, neither nitrate nor nitrite remaining.

4. *Oxidation of Ammonia to Nitrate.*—Solutions of various compositions were employed, in all of which the addition of a little soil pro-

duced active nitrification. Nearly all the organisms already enumerated were sown in one or other of the solutions, and some in several different solutions. In no case was nitrification certainly observed. Minute traces of nitrate were in some instances found, but these always failed to increase. The author now proposes to commence a systematic study of the organisms contained in soil.

Discussion.

Dr. Percy Frankland said that he also had so far searched in vain for the nitrifying organism; but he could not agree that no one had been successful. Heræus had succeeded in isolating two or three organisms which were stated not only to induce the formation of nitrite in urine solutions, but also in mineral solutions containing ammonium salts. He had, however, himself shown that Heræus was undoubtedly wrong in attributing nitrifying powers to a number of organisms, his mistake arising from his ignorance of the fact that nitric acid is normally present in urine. The effects of organisms in milk had been very fully described by Hueppe, who had shown that coagulation might take place independently of the presence of acid. He was not satisfied with the method adopted by Mr. Warington for sterilising milk—perhaps the most difficult of all fluids to sterilise; sterilisation might, however, be effected by heating on five successive days at a temperature of 65—70°—and it had long been known that milk so treated differed from steam-sterilised milk. Had Mr. Warington repeated the experiments sufficiently often to be sure of the results being constant? micro-organisms were often extremely capricious in their chemical action. Thus, under certain conditions, *M. prodigiosus* entirely changed its character—becoming colourless, but the colourless form would regain the pigment-producing power on changing the cultivating medium.

Mr. Warington in reply said that he was under the impression that Heræus had found nitrification to take place only in those cases in which soil was introduced into the experimental fluids. The results he had obtained when using milk were perfectly constant, and he had met with no failures in sterilising; this probably was attributable to the fact that he had used fresh country milk milked directly into sterilised bottles. He had observed the change in colour of *M. prodigiosus*, but Dr. Klein, to whom he submitted his cultures, had found that the forms were distinct, and that only white organisms could be obtained from the pure white form.

46. "The optical and chemical properties of Caoutchouc." By J. H. Gladstone, Ph.D., F.R.S., and Walter Hibbert, F.I.C.

This is an extension of the observations on caoutchouc published in

Dr. Gladstone's paper on Essential Oils (*Chem. Soc. Trans.*, 1886, 609). The substance experimented on was obtained from the best commercial Para rubber. Many attempts were made to separate the two supposed modifications, and to remove an oxidised product. The most promising method seemed to be to dissolve the rubber in cold chloroform, and precipitate partially with a little alcohol, but no good separation was effected, and the results of analysis gave usually about 3 per cent. of oxygen. One small specimen, very carefully prepared and dried, contained carbon and hydrogen in almost exactly the proportions $C_{10} : H_{16}$, with only 0·5 per cent. deficiency.

Optical analyses are given of 17 preparations dissolved in benzene. They were prepared from different specimens in different ways, and variously dried, and two of them were second precipitates from chloroform or ether solutions. The refraction and dispersion equivalents vary considerably, but they all agree in showing that the $C_{10}H_{16}$ must have more than one pair of carbon-atoms doubly linked. All the dispersion equivalents, and 11 of the refraction equivalents also exceed what theory requires for two pairs of carbon-atoms so combined, namely, refraction equivalent, 75·2, and dispersion equivalent, 4·8. They fall short of what would be required by three pairs, at any rate in the case of refraction (theory, refraction equivalent, 77·4, and dispersion equivalent, 5·6), but the presence of a little oxygen in the substance examined would reduce the refraction and dispersion considerably. The observations on the best specimen already described give the highest figures, the mean of which are, refraction equivalent, 77·23, and dispersion equivalent, 5·50. There is little doubt, therefore, that the main constituent of caoutchouc is a compound which has three pairs of carbon-atoms doubly linked. If this be the case, the molecular formula cannot be C_5H_8, like isoprene, or $C_{15}H_{24}$, like cedrene, as these would give respectively one and a-half and four and a-half pairs of carbon-atoms, united by double linking. It cannot contain the hexagonal ring, but must be expressed graphically by a chain formula. This may account for the wide difference of properties between caoutchouc and the various essential oils.

The action of the halogens on caoutchouc dissolved in chloroform was examined. Chlorine gave rise to a substance which could be obtained in yellow scales, the best preparation giving figures which seem to point to $C_{10}H_{14}Cl_8$. Bromine in weak solution acts upon caoutchouc in chloroform, and by volumetric methods it was determined that 136 grams of the caoutchouc used combine with 303 grams of bromine on an average, which indicates $C_{10}H_{16}Br_4$ as the first product of the action. The prolonged action of bromine causes the separation of hydrogen bromide, and the formation of a compound precipitable by ether as a white solid, $C_{10}H_{15}Br_5$. It seems not impro-

bable that this is formed from a compound, $C_{10}H_{16}Br_6$, by the elimination of HBr. Iodine has no action.

The action of heat was also studied. The caoutchouc hydrocarbon dissolved in toluene remains unchanged optically on exposure to a temperature of 200°.

As is known, the various oils given by dry distillation contain carbon and hydrogen in the same proportions as the original caoutchouc, but the structural re-arrangement is most materially modified, as indicated by the following optical constitutional formulæ :—

Caoutchouc ..	$n C_6''C_1H_{16}$,	Caoutchene ..	$C_4''C_6H_{16}$,
Isoprene	$C_4''CH_8$,	Heveene	$nC_2''C_3H_8$.

47. "An Apparatus for maintaining a constant pressure when distilling under reduced pressure." By W. H. Perkin, F.R.S.

The essential parts of the apparatus are a barometer tube in connection with the exhausted apparatus, and a valve through which air is admitted when by the action of the pump the pressure becomes reduced below the prescribed point. A copper rod armed with a platinum point passes through the upper end of the barometer tube and can be adjusted at any desired height; so soon as the mercury rises and touches the point of the rod, an electric circuit is completed and the valve is raised and air admitted. The valve is a glass sphere in a glass seating, the sphere being suspended from the armature of an electromagnet; the sphere has a weight attached to it which causes it at once to fall back when the circuit is broken. Even under a pressure of 60 mm.—the lowest obtained with the water-pump used—the apparatus renders it possible to maintain the pressure constant to within a millimetre.

At the next meeting, on June 21st, the following papers will be read :—

"Chlorofumaric and Chloromaleic Acids." By W. H. Perkin, F.R.S.

"Combustion by means of Chromic Anhydride." By C. F. Cross and E. J. Bevan.

"The Sulphonation of Metaxylene." By G. T. Moody, D.Sc.

"Researches on Naphthalene-derivatives." By Dr. Armstrong and W. P. Wynne.

"A New Method for the preparation of mixed Tertiary Phosphines." By J. N. Collie.

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CHEMICAL SOCIETY.

No. 56. Session 1888–89.

June 21st, 1888. Mr. W. Crookes, F.R.S., President, in the Chair.

Messrs. George Embrey and Albert L. Guiterman, Ph.D., were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. John Burke Fairley, 2, Sidney Villas, Lower Eglinton Road, Shooter's Hill; A. Alexander Ramsay, Auckland, New Zealand; C. Heinrich Trinks, 117, King Henry's Road, N.W.

The following were elected Fellows of the Society:—Messrs. John Alexander, Charles Bradshaw, Lewis Edmunds, William Humphrey Gibson, Joseph Henry Maiden, Henry Alexander Miers, M.A., Frank Mousley, James H. Rymer Paterson, George Woodyatt Procter, Herbert W. Seely.

The following papers were read:—

48. "Chlorofumaric and Chloromaleic Acids and their Magnetic Rotatory Powers." By W. H. Perkin, Ph.D., F.R.S.

The author has further studied the action of phosphorus pentachloride on tartaric acid, first examined by Mr. Duppa and himself in 1861. The main product is the chloride of *chlorofumaric acid*, not chloromaleic chloride as was formerly supposed. In the paper, the properties of the chloride are described, and also those of the acid and of its acid potassium, ammonium and ethylic salts. On treatment with ammonia the ethylic salt is first converted into the ethylic salt of chlorofumaramic acid, $CO(NH_2)\cdot CH\cdot CCl\cdot CO_2Et$, a substance already described by Claus and Voeller as a maleic compound; on further treatment with ammonia, amidofumaramide is produced; this crystallises in pale yellow needles, and decomposes when heated,

no definite fusing point being observable. Claus and Voeller operating in the same manner have, however, obtained a substance which, although of the same composition, crystallises in colourless scales melting at 122°.

On heating a mixture of chlorofumaric acid and chlorofumaric chloride, chloromaleic anhydride is obtained: this substance is dimorphous, being obtainable in hard crystals melting at 34·5°, and as a solid which melts just below 0°. Chloromaleic acid and a number of its salts are fully described in the paper; like the maleates the chloromaleates yield a brown-red coloration with ferric salts, while the chlorofumarates like the fumarates afford a buff precipitate with ferric salts. The magnetic rotatory powers of a number of the compounds described are recorded in the paper.

49. "Combustion by means of Chromic Anhydride." By C. F. Cross and E. J. Bevan.

Ladenburg in 1865 described a method of ultimate analysis of carbon compounds, consisting in heating with iodic acid and sulphuric acid in sealed tubes; the oxidation was found complete for a satisfactory variety of substances, and the experimental numbers obtained showed the process to be available as a laboratory method of estimating carbon and hydrogen.

The authors have investigated the action of chromic anhydride in presence of sulphuric acid on carbon compounds. Ladenburg mentions this "combustion mixture," but regards it as unavailable for quantitative determinations on account of the CrO_3 decomposing with evolution of oxygen. This, however, is shown by the author's experiments to take place to so small an extent under the conditions as to time and temperature of a combustion that it may be neglected.

The action of the mixture has been investigated under atmospheric pressure in vessels connected with a gas collecting and measuring apparatus. The carbon of the celluloses and carbohydrates is entirely converted into gaseous products. Some typical benzenoid compounds have also been investigated, and the results indicate that complete oxidation may be effected. The monobasic acids of the fatty series on the other hand are not completely resolved, and the results are consequently variable. Amide and imide nitrogen prevent complete oxidation; one of the causes probably being that urea is not attacked by the mixture. Compounds containing negative radicles such as Cl, Br, S and NO_2 have not been investigated.

Discussion.

Mr. A. H. Allen said that he had been in the habit for years of

using chromic anhydride for oxidising carbon in steel, but he had found that some carbon dioxide was always evolved when pure sulphuric acid and the commercial anhydride were used; he therefore prepared the solution of the anhydride from fused lead chromate and sulphuric acid.

50. "Metaxylenesulphonic Acids." By G. T. Moody, D.Sc.

According to Jacobsen, metaxylene yields two sulphonic acids; the 1 : 3 : 4 modification is the chief product, the 1 : 2 : 3 modification being also formed, and in larger quantity when the temperature during sulphonation is low. The primary object the author had in view was to ascertain if the 1 : 2 : 3 acid was convertible by isomeric change into the isomeride, the investigation being one of a series which are being carried on in the Central Institution laboratory for reasons briefly stated by Dr. Armstrong in Abstract No. 99, 1887.

The author arrives at the conclusion that the contradictory results obtained by Jacobsen, Remsen, and others on sulphonating metaxylene are to be explained by the fact that in their investigations they did not use a pure hydrocarbon. Metaxylenesulphonic acid, obtained by sulphonating crude metaxylene, may be freed from paraxylenesulphonic acid and other impurities, by *repeatedly* crystallising it from sulphuric acid diluted with one-third its weight of water in the manner described by Jacobsen, who, however, clearly did not carry the purification far enough. The pure sodium salt differs greatly from the description of it given by Jacobsen (*Berichte*, 1878, 17). It crystallises in beautiful tables belonging in all probability to the anorthic system, and contains one molecule of water of crystallisation. When hydrolysed the pure sodium salt yields a hydrocarbon which on sulphonation with chlorosulphonic or sulphuric acid gives *only one* sulphonic acid, the sulphonamide prepared from which melts at 137°.

Jacobsen's sulphonamide melting at 95—96° is not a derivative of metaxylene at all, but a mixture containing a considerable quantity of paraxylenesulphonamide; the solid xylenol obtained from it by Jacobsen being identical with paraxylenol, which he describes in the same paper.

Dibromometaxylenesulphonic acid, on reduction with zinc-dust and sodium hydroxide, yields a sulphonic acid the barium salt of which crystallises in large prisms, the sulphochloride in prisms melting at 39°, and the sulphonamide in slender, brittle needles melting at 113°. Jacobsen and Weinberg obtained this sulphonamide in an impure condition (*Berichte*, 1878, 1534), and regarded it as identical with that melting at 95—96° obtained by Jacobsen on sulphonating "metaxylene" with sulphuric acid.

If the sulphonic acid giving the sulphonamide melting at 113° be heated at 100°, isomeric change readily occurs, and the acid corresponding to the amide melting at 137° is formed.

The author proposes to closely study the derivatives of the acid yielding the amide melting at 113°.

51. "The Formation of Isomeric Toluenesulphonic Acids." By Hugh Gordon, B.A.

The object which the author has had in view was similar to that by which the author of the previous communication was guided. It is well known that when toluene is sulphonated at low temperatures a large proportion of ortho-acid is obtained, whereas if sulphonation be effected at a temperature near the boiling point of toluene the para-acid is the almost exclusive product; it is obviously important, if possible, to determine whether or no the para-acid is formed from the ortho-acid by simple isomeric change. The author finds that toluene-orthosulphonic acid (hydrated) is not affected by heating at 100°, but by somewhat prolonged heating at 140—150° it is converted into the para-acid; and inasmuch as this temperature is far above that at which toluene boils, it appears improbable that the ortho-acid becomes hydrolysed and that the para-acid is formed by resulphonation of the toluene at a high temperature. The results as yet obtained are regarded, however, as incomplete, an extended investigation of the behaviour of the various sulphonic acids both of toluene and of toluene-derivatives being in progress.

52. "A New Method for the Preparation of Mixed Tertiary Phosphines." By Norman Collie, Ph.D.

The author has already called attention to the way in which when heated compound phosphonium chlorides decompose into the chlorhydride of the tertiary phosphine and an olefine. He has since used this as a method for the preparation of mixed tertiary phosphines. Triethylphosphine has been united with methyl, propyl, amyl and benzyl chlorides respectively; all these compound phosphonium chlorides when heated decompose in a manner similar to the tetrethylphosphonium chloride, yielding ethylene and chlorhydrides of the tertiary phosphines.

The tertiary phosphines were prepared from the chlorhydride by the action of caustic soda. In this manner the following phosphines have been obtained:—Methyldiethylphosphine, dimethylethylphosphine, propyldiethylphosphine, amyldiethylphosphine, benzyldiethylphosphine and dibenzylethylphosphine.

53. "Some Interactions of the Halogen Hydrides." By G. H. Bailey and G. J. Fowler.

The authors have found that when phosphorus pentoxide is exposed to hydrogen chloride gas at ordinary temperatures, large quantities of the gas are taken up by it, amounting to nearly a quarter of a litre per gram of the pentoxide, the gas and the pentoxide interacting chemically: $2P_2O_5 + 3HCl = POCl_3 + 3HPO_3$.

A similar interaction occurs with hydrogen bromide, but none with hydrogen iodide. They have also observed that though hydrogen chloride has no action on mercury, yet if mixed with oxygen it readily attacks the mercury, forming an oxychloride, $Hg_2OCl_2{\cdot}HgO$, action taking place even in the dark. With hydrogen bromide gas and oxygen the interaction is more rapid, but whereas in the case of the chloride the whole of the hydrogen is oxidised to water, in the case of the bromide a large proportion remains uncombined. Hydrogen iodide gas forms with mercury mercurous iodide or mercuric iodide, according as the mercury or the iodide is in excess.

54. "Remarks on the Paper of Drs. Japp and Klingemann on the Constitution of certain so-called Mixed Azo-compounds." By Prof. Victor Meyer.

From a note on page 523 of the above-named article (*Chem. Soc. Trans.*, 1888), I see that Messrs. Japp and Klingemann regard my "Nachschrift," in the *Berichte* (1888, p. 18), as a claim of priority on my part. On re-perusing the article I see that the wording, quite unintentionally on my part, permits of such a reading. I therefore hasten to explain that the results there referred to were arrived at by Messrs. Japp and Klingemann and myself independently, and that without doubt they obtained theirs ere I did mine. Nothing is further from my thoughts than the desire to detract from the merits of these workers, especially in a field which they have enlarged by such valuable and successful investigations.

55. "The Action of Potassium on Tetralkylammonium Iodides." By C. M. Thompson and J. T. Cundall.

According to Weyl, if potassium in solution in liquid ammonia act on ammonium chloride, ammonium is produced and dissolves in the ammonia, forming a blue solution; this statement lacks confirmation, and has even been contradicted. In the hope of obtaining more decisive results, the authors have substituted tetramethyl- and phenyltrimethyl-ammonium iodide for ammonium chloride, but unsuccessfully. The greater part of the former was unchanged, a portion only

being acted on by the potassium giving potassium iodide, ethane and trimethylamine; from the latter, potassium iodide, dimethylaniline and trimethylamine were obtained.

56. "The Solubility of Isomeric Organic Compounds in Relation to their Fusibility." By Thomas Carnelley, D.Sc., and Andrew Thomson, D.Sc., M.A., University College, Dundee.

Seven years ago (*Phil. Mag.* [5], **13**, 180) one of the authors showed that the fusibility and solubility of isomeric compounds were very closely related to one another, so that of two or more isomeric bodies, that dissolves the most easily which has the lowest melting point and in which the atomic arrangement is the least symmetrical. At that time the investigation had included only a comparatively small number (58) of compounds. The authors have now extended the investigation, so as to include all isomeric sets of carbon compounds whatever. Their data have been obtained partly from literature and partly as the results of their own determinations. The following are their general conclusions:—

(1.) For any series of isomeric carbon compounds the order of solubility is the same as the order of fusibility, *i.e.*, the most fusible compound is also the most soluble. This rule has been applied in 1778 cases of which 1755 accord with the rule, including all kinds of isomers, from the most simple to the most complicated. There are only 23 exceptions, and a large proportion of these is of a very doubtful character.

(2.) The order of solubility of the corresponding salts of any series of isomeric organic acids is the same as that of the acids themselves, *i.e.*, the salts of the more soluble and more fusible acids are also more easily soluble than the corresponding salts of the less soluble and less fusible acids; and if fusible more easily fusible, but the melting points of most organic salts cannot be determined because they decompose before fusion. To this rule there are five exceptions out of 143 cases in which the rule can be applied, and as regards at least three of these it is very doubtful whether they are real exceptions.

(3.) The order of solubility of two or more isomeric compounds is independent of the nature of the solvent. This rule can be applied in no less than 666 cases, and among these there is not a single exception. The truth of the rule has also been proved more particularly in the case of meta- and para-nitraniline, the solubility of each of which in 13 different solvents has been carefully determined.

(4.) The ratio of the solubility of two isomers in any solvent is constant, and is independent of the nature of the solvent; this has

been proved as yet only in the case of the meta- and para-nitranilines in respect of 13 different and very varied solvents.

The extremely close and intimate relation of solubility to fusibility, however, is proved not only by the very large number of cases of isomeric compounds which the authors have examined (nearly 2000), but also by the relative fusibility and solubility of the various allotropic modifications of the same element (*e.g.*, P, S (?), Se), and of mixtures of organic compounds (*e.g.*, solid paraffins), and of inorganic salts (*e.g.*, sodium and potassium nitrates), in all of which it is pointed out that the order of solubility is the same as the order of fusibility, and that this order is independent of the nature of the solvent.

The curve of the solubility of mixtures of sodium and potassium nitrates in various proportions is very striking. Starting with pure sodium nitrate, the solubility increases and the curve rapidly falls as the percentage of $NaNO_3$ diminishes and that of KNO_3 increases, until the proportion of the latter amounts to about 20 per cent.; the solubility then remains constant and the curve becomes a horizontal line until the proportion of the potassium salt reaches about 40 per cent., after which the solubility diminishes and the curve rapidly rises until pure KNO_3 is reached. The curve of fusibility falls rapidly from pure $NaNO_3$, until the latter amounts to 50 per cent., after which it remains constant until the KNO_3 equals 60 per cent., and then rises rapidly until pure KNO_3 is reached.

57. "Notes on some Compounds of Chromium." By Sydney Lupton, M.A.

The determination of the atomic weight of chromium has occupied the attention of many chemists, but from a variety of causes the results obtained are far from satisfactory. In some cases single experiments are relied on, and in others proper attention has not been paid to the solubility of silver chloride in solutions of chromic chloride, the great difficulty of drying chromic sulphate without decomposition and of completely decomposing it by heat, the liability of barium chromate to carry down other salts, or to be carried down by barium sulphate. Hence the true atomic weight cannot be considered to be determined to within about 1 per cent. In fact Clarke, placing apparently great reliance on a single experiment of Siewert's, takes Cr = 52·01; while Meyer and Seubert, giving greater weight to the experiments of Berlin, assume Cr = 52·45, which is practically the value preferred by Fresenius.

The following experiments were made with the object of suggesting a method for the determination of the atomic weight of chromium free from the defects inherent in all the methods which have hitherto

been used. Incidentally a few old results have been either confirmed or rendered doubtful.

Potassium Dichromate.—The density of this salt was found by Thomson to be 1·98, which is copied into such authorities as *Wurtz's Dictionnaire* and *Biedermann's Chemiker Kalendar*, 1884. Karsten found 2·6; *Miller's Elements* gives 2·62; Schröder found about 2·7. The density of some small crystals of the twice recrystallised salt was determined in benzene, the air being removed by a small hand-pump; it was found to be (i) 2·69, (ii) 2·67.

Ammonium Dichromate.—The density is given by Clarke as 2·151. Three experiments in benzene, the air being removed by a small pump, gave (i) 2·16, (ii) 2·18, (iii) 2·75, and one in chloroform (iv), 2·18.

100 grams of water dissolve—

At	7·0°	about	23 grams of the salt;	at	60°	about	82 grams.
,,	10·0	,,	24 ,,		94	,,	115 ,,
,,	16·5	,,	28 ,,		107	,,	173 ,,
,,	18·0	,,	33 ,,				

The solution boils at 107° C.; it density is 1·12 at 10°, and 1·158 at 18° C.

The finely powdered salt is easily dried at 110° in the air-bath.

Darby states (*Jour. Chem. Soc.*, i, 20) that ammonium dichromate decomposes suddenly when heated to 200°. A small quantity of the dry powdered salt was heated in a thin test-tube, with a thermometer inside placed in a paraffin bath. Sudden decomposition took place at (i), 228° C.; (ii), 230° C.

Since the composition of the salt has been placed beyond doubt by Siewert (*Jahresb.*, 1862, 148), the ignition of ammonium dichromate and the determination of the chromic oxide left seems in theory to afford an unexceptionable method of determining the atomic weight; but the difficulty of avoiding loss of oxide by the sudden rush of the gas is very great. Darby used tubes plugged with cotton-wool, Richmond and Abel tubes plugged with asbestos, and I have tried mixing the salt with a large excess of ignited silica without success. Hence it seemed advisable to reduce the salt previous to ignition to obtain the oxide. The reduction with hydrogen dioxide is rather tedious, and it is somewhat difficult to obtain a solution of the dioxide which leaves no residue on ignition. A solution of sulphur dioxide was therefore used as the reducing agent. 0·1539 gram of ammonium dichromate was dissolved, reduced by sulphur dioxide, evaporated, and the residue heated for two hours at 200°, when the residue weighed 0·3228 gram, which was reduced to 0·3218 gram by further heating during an hour and a half; this residue nearly corresponds to the formula $Cr_2 3SO_4 7H_2O$. After long-continued heating over a good

argand, the residue consisted of a mixture of sulphate and oxide, which, when heated over a bunsen to bright redness for two and a half hours, gave a residue weighing 0·1021 gram, which remained unchanged after heating for another hour. Hence, one part of ammonium dichromate left 0·6634 part of residue, the formula of which would be about $Cr_2 3SO_4 15Cr_2O_3$, instead of 0·60 required for Cr_2O_3. A second experiment gave similar results, and even prolonged ignition over a gas blowpipe failed to produce the mass to oxide. This difficulty in drying chromic sulphate, and in decomposing it by heat, explains the high value Cr = 53·563 obtained by Moberg by the ignition of chromic sulphate and of ammonio-chromic alum. Reduction with (i) hydrogen oxalate, (ii) alcohol and hydrogen nitrate, (iii) alcohol and hydrogen chloride is liable to occasion loss by spitting.

Mercurous Chromates.—These salts have been investigated by Vauquelin, Godon, Gmelin, Darby and Treese, but the results obtained are not very concordant. On pouring potassium dichromate into mercurous nitrate slightly acidulated with nitric acid, a heavy orange-red precipitate falls. Gmelin states that on heating this salt, Godon obtained 0·126 part, and he himself 0·1232 part of oxide. One part of $Hg_2O{\cdot}4Hg_2CrO_4$ when heated would leave about 0·1232 part of oxide. According to Darby, the precipitate is of the composition $Hg_2O{\cdot}3Hg_2CrO_4$, but he does not state that he himself analysed it. It is slightly soluble in water, and easily soluble in hot dilute nitric acid from which it separates on cooling as the normal salt Hg_2CrO_4. From one part of this salt Darby obtained by ignition (i) 0·1463, (ii) 0·1488, (iii) 0·1479 part of chromic acid. *Wurtz' Dict.*, **1**, 896, assigns to Godon and Gmelin's salt the formula $Hg_2OHg_2CrO_4$, and Treese (*Zeit. f. Chemie* [2], **6**, 30), states that the salt thus obtained is normal and not decomposed by water.

1·7234 gram of mercurous chromate obtained from Messrs. Hopkin and Williams were heated over a bunsen burner until a dull green residue weighing 0·1943 gram was left. The ratio is 1 : 0·1127, and a second experiment, in which a slight loss occurred, gave 1 : 0·1118. This corresponds fairly to the salt $Hg_2O{\cdot}3Hg_2CrO_4$ containing a little impurity or traces of mercurous oxide.

A hot solution of potassium dichromate was poured into a hot solution of mercurous nitrate slightly acidulated with hydrogen nitrate. The fine heavy orange precipitate was washed, dried on the water-bath, and heated at 120° C., until it ceased to lose weight. Four experiments on the ignition of this salt gave the ratios :—

(i.) 1 : 0·1523	(iii.) 1 : 0·1516
(ii.) 1 : 0·1517	(iv.) 1 : 0·1510

This powder then appears to be normal mercurous chromate containing a small proportion of either mercuric chromate or mercurous dichromate. A quantity of it was boiled for some time with dilute nitric acid and the undissolved residue was washed and dried. 1·5525 gram left on ignition 0·2294 gram of oxide, corresponding to the ratio 1 : 0·1477. Hence the undissolved residue seems to be normal mercurous chromate, Hg_2CrO_4.

In conclusion, two methods for the determination of the atomic weight of chromium seem to suggest themselves :—

1st. The reduction of ammonium dichromate at a low temperature by a weak solution of hydrogen oxalate, or of some similar reducing agent, and the determination of the chromic oxide left on ignition.

2nd. The ignition of normal mercurous chromate and determination of the chromic oxide.

In the first case the required atomic weights are well known, but the purification of the dichromate is tedious, and the reducing agent causes additional chance of error. In the second case the chromate is more easily purified, but the results will be affected by the uncertainty still attaching to the atomic weight of mercury.

58. "The Estimation of Alumina and Free Sulphuric Acid in Alum Cake and Sulphate of Alumina." By Rowland Williams.

The author recommends Chancel's method of estimating alumina by boiling with sodium thiosulphate (*Watts' Dictionary*, **1**, 155) as more accurate and expeditious than the ammonia process. In support he quotes the following results :—

	"Ammonia" method.	"Thiosulphate" method.	Theory.
Alums (pure).			
Potash alum.....	11·01	10·76	10·81
Ammonia alum	11·50	11·24	11·31
Alum Cakes.			
No. 1 sample	12·94	12·66	—
No. 2 „	12·34	12·21	—
No. 3 „	12·93	12·42	—
Sulphates of Alumina.			
No. 1 sample	12·95	12·75	—
No. 2 „	13·51	13·21	—
No. 3 „	13·33	13·12	—
No. 4 „	14·62	14·41	—
No. 5 „	15·11	15·01	—
No. 6 „	14·81	14·68	—

The estimation of the free acid in alum cake, &c., is best effected by the following process :—300 grains of the sample are weighed into a stoppered bottle, and 1200 grains measure of strong alcohol added, the contents of the bottle being frequently shaken, and the digestion allowed to proceed all night. The next morning the alcohol is filtered off, and 800 grains measure of the filtrate (equal to 200 grains of the sample) titrated with decinormal caustic soda. Experiment shows that the alcohol does not extract other matters besides sulphuric acid which are liable to affect the result. To further test the accuracy of the method, ordinary sulphate of alumina was freed from sulphuric acid by washing with alcohol, and known amounts of acid were then added, and the amount estimated by the process described; the results were as follows :—

Percentages of Free Sulphuric Acid.

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
Added	0·73	1·22	0·98	0·49	0·59
Found	0·69	1·19	0·96	0·44	0·54

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Minerals of New South Wales. By A. Liversidge, London 1888 From the Author.

Argentiferous Lead Smelting at Leadville. By A. Guyard. (Extract from U.S. Geological Survey, Monograph XII.) From F. D. Emmons, Esq.

An Elementary Text-Book of Practical Metallurgy. By A. R. Gower. London 1888. From the Publishers.

Nature's Hygiene. By C. T. Kingzett. Third edition. London 1888.

Manual of Practical Assaying. By J. Mitchell, edited by W. Crookes. 6th Edition, London 1888. From the Editor.

Elementary Text-Book of Practical Metallurgy. By A. R. Gower, London 1888. From the Author.

II. *By Purchase.*

I tesori sotterranei dell' Italia. Per G. Jervis. 3 Tomi. Roma, Torino, Firenze 1873–1881.

Abriss der chemischen Technologie mit besonderer Rücksicht auf Statistik und Preisverhältnisse. Von C. Heinzerting. Cassel and Berlin 1888.

Muspratt's Chemie in Anwendung auf Künste und Gewerbe, frei bearbeitet. Von F. Stohmann and B. Kerl. Vierte Auflage. Erster Band. Braunschweig 1888.

A Text-Book of Human Physiology, including Histology and Microscopical Anatomy; with special reference to the requirements of Practical Medicine. By L. Landois. Translated from the fifth German edition, with additions by W. Stirling. Two vols. London 1886.

The Gas Engineer's Chemical Manual. By J. A. Wanklyn. Second edition. London 1887.

Jahrbuch für Elektrotechnik für das Jahr 1887. Herausgegeben von G. Krebs and C. Grawinkel. Heft I. Halle a. S. 1888.

Notes on Qualitative Analysis, Concise and Explanatory. By H. J. H. Fenton. Cambridge 1888.

Factoren-Tabellen. Von J. Dos s. e. Silva. Braunschweig 1887.

Lavoisier, 1743–1794, d'après sa correspondance, ses manuscrits, ses papiers de famille, et d'autres documents inédits. Par E. Grimaux. Paris 1888.

Asbestos, its Production and Use. By R. H. Jones. London 1888.

Applications of Dynamics to Physics and Chemistry. By J. J. Thomson, London 1888.

Soaps and Candles. Edited by J. Cameron, London 1888.

La constitution des alcaloïdes végétaux. Par A. Pictet, Paris 1888.

Die Fabrikation von chlorsaurem Kali und anderen Chloraten. Von K. W. Jurisch, Berlin 1888.

HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY, ST. MARTIN'S LANE.

ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 57. Session 1888–89.

Titles of Papers received and printed in Transactions during the recess.

59. "The Vapour-density of Hydrofluoric Acid." By T. E. Thorpe, F.R.S., and F. J. Hambly. (Preliminary Notice.)

60. "Thiophosphoryl Fluoride." By T. E. Thorpe, F.R.S., and J W. Rodger. (Preliminary Notice.)

61. "The Action of Bromine on Potassium Ferricyanide." By Edgar J. Reynolds.

62. "Some Amines and Amides derived from the Nitranilines." By Raphael Meldola, F.R.S., and E. H. R. Salmon.

63. "The Rotatory Power of Benzene-derivatives." By J. Lewkowitsch, Ph.D.

64. "The Action of Chromium Oxychloride on Ortho-substituted Toluenes." By Charles M. Stuart, M.A., and W. J. Elliott.

65. "The Molecular Weight of Iodine in its Solutions." By Morris Loeb, Ph.D.

66. "The Use of Aniline as an Absorbent of Cyanogen in Gas Analysis." By Morris Loeb, Ph.D.

67. "Two new Chlorides of Indium, and on the Vapour-densities of Indium, Gallium, Iron and Chromium Chlorides." By L. F. Nilson and Otto Pettersson.

68. "Some Derivatives of Anthraquinone." By A. G. Perkin, and W. H. Perkin, Jun., Ph.D.

69. "The Influence of Silicon on the Properties of Iron and Steel." Part II. By Thomas Turner, Assoc. R.S.M., F.I.C.

70. "The Isonitrile of Phenylhydrazine." By S. Ruhemann, Ph.D., and W. J. Elliott.

71. "Researches on Silicon Compounds and their Derivatives. Part III. The Action of Silicon Tetrabromide on Allyl- and Phenylthiocarbamides. Part IV. The Action of Ethyl Alcohol on the Compound $(H_4N_2CS)_8SiBr_4$." By J. Emerson Reynolds, M.D., F.R.S.

November 1st, 1888. Mr. W. Crookes, F.R.S., President, in the Chair.

Messrs. James Schleselman and Henry A. Miers were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Charles M. Adams, 29, Mosley Street, Newcastle-on-Tyne; John Hope Belcher, B.A., Craigmount, Edinburgh; Percy Carter Bell, The Cliff, Higher Broughton, Manchester; William Berry, Hampton Park, Redland, Bristol; William D. Bohm, 51, The Avenue, Acton; Frank Bower, 37, Lansdowne Road, Clapham Road, S.W.; James E. Brunker, Minore, Saint Kevin's Park, Rathmines, Dublin; George Alexander Byrn, Technical College, Sydney; John Morrow Campbell, 22, Regent Moray Street, Glasgow; Vaughan Cornish, B.Sc., High School, Newcastle-under-Lyme, Staffs.; William Douglas, A.I.C., Diamond, Demerara; Arthur G. Everard, North Street, Bishop's Stortford, Herts; Henry Forth, 1, Beech Avenue, Sherwood Rise, Nottingham; Frederick B. Guthrie, 65, Portland Road, Notting Hill, W.; John Lawrence Van Guyzel, Indian Medical Service, Madras; John Hansfield, Waterfoot, near Manchester; Urban Arthur Jackson, 2, New Bridge Street, Strangeways, Manchester; Alfred Battye Knaggs, Ebor Mount, Huddersfield; Oscar Lowman, B.A., Ph.D., 66, West 8th Street, Cincinnati, Ohio; William Marshall, The Baths, Saint Andrews, N.B.; George Edward Perry, 6, Norwood Villas, Edgbaston, Birmingham; Hubert Naylor Bardsley Richardson, Elmfield, Knighton, Leicester; John S. Rigby, Bagot Street, Liverpool; John Sanderson, 57, Belsize Park Gardens, London, N.W.; Thomas Oliver Landolt, Baron's Court Road, West Kensington; William Jay Schieffelin, Areis Strasse, 1, Munich; Arthur Landaner Stern, Bass & Co's. Old Brewery, Burton-on-Trent; William Taylor, Hong Kong; Charles Turner, 25, Sidney Street, Cambridge; J. T. Ainslie Walker, Hope Cottage, Winch-

burgh, Linlithgowshire; Edward Dalrmyple Walroud, B.A., North Eastern County School, Barnard Castle, Durham; Frederick Walmesley Warrick, 136, Southampton Row, W.C.; Edward J. Way, Transvaal Gold Exploration Company, Transvaal; Ernest William Whieldon, 42, Worthingham Road, East Dulwich; R. W. Woosnam, York House, Southend-on-Sea.

The following papers were read :—

72. "The Constitution of the Terpenes and of Benzene." By William A. Tilden, D.Sc., F.R.S.

With the object of testing further the current hypothesis concerning the constitution of the terpenes, the author has made a series of quantitative estimations of the amount of paratoluic acid produced by the oxidation of several of the terpenes with dilute nitric acid in comparison with the amount of the same product formed under the same condition from cymene and from paraxylene. The following results were obtained :—

100 parts by weight give of paratoluic acid—

Cymene (from turpentine)	80·1
Cymene (from cumin oil)	73·1
Paraxylene (Kahlbaum's)	77·2
Australene from American turpentine.....	1·2
Terebenthene from French turpentine.....	1·9
Hesperidene from orange oil.....	0·0
Dipentene from $C_{10}H_{16}$·2HCl obtained from terpin	27·6

An experiment on a larger scale with hesperidene showed that the chief product of its oxidation by nitric acid is oxalic acid: using chromic acid mixture, Wright and Beckett found that acetic acid was the only product.

The characteristic properties of the terpenes as a class,—the readiness with which they polymerise by heat or contact with a small quantity of sulphuric acid, the eagerness with which they combine with bromine, with hydracids, and in some cases with the elements of water, and the nature of their products of oxidation,—are such that they differ wholly from all known benzenoid hydrocarbons.

In order to settle the limit of the combining capacity of the chief terpenes about which there is some difference of statement on the part of different authors, the amount of bromine taken up by the hydrocarbon was determined. From the several experiments made in each case the following numbers were deduced.

136 parts or 1 mol. proportion of the hydrocarbon combines with the following quantities of bromine :—

Australene	313
Terebenthene	307
Hesperidene	322
Dipentene (terpilene)	297

Calculated for Br_2 160; for $2Br_2$ 320.

In all cases the hydrocarbon unites with 4 atoms of bromine and no more. Camphene does not combine with bromine and hence must be regarded as saturated in the usual sense.

Since the terpenes possess at most four units of available combining capacity, the nucleus of 6 carbon-atoms, which they all undoubtedly contain, cannot be supposed to form an open chain. They must be united into a closed chain containing at the most two double bonds. Hence formulæ of the character of those proposed originally by Oppenheim, and later by Goldschmidt and Zurrer, by Wallach and Brühl are the most probable. Such formulæ represent the molecule as constructed upon the basis of a ring of 6 carbon-atoms disposed in the manner which has been so long familiar in Kekulé's formula for benzene. But since the terpenes are certainly not benzene-derivatives, Kekulé's formula must be abandoned. The evidence in support of this conclusion is not derived solely from the foregoing considerations; which standing alone would probably be regarded as inconclusive. The chief objection which has been urged against Kekulé's formula is based upon the difference in the nature of the link between the carbons which stand in the relative positions 1 : 2 and 1 : 6. The hypothesis devised by Kekulé himself to meet this difficulty cannot be regarded as satisfactory. Another objection to the symbol is that benzene is represented as containing "ethylenic" carbon, for which there is no evidence at all; moreover a body of this formula when treated with nitric acid ought to yield abundance of oxalic acid: this the terpenes do, but the benzenoid hydrocarbons do not.

The characteristics of the benzenoid hydrocarbons and their derivatives may be explained by the formulæ proposed by Claus, by Ladenburg, and by Armstrong and von Baeyer, but at present there is not sufficient evidence to enable us to decide between them.

As to the terpenes, the conclusions derived from their refraction equivalents are so much at variance with the chemical behaviour of many members of the group, that they cannot be accepted without considerable qualification. Such other physical evidence as is deducible from the work of Hartley, and of Abney and Festing, tells entirely against the assumption that the terpenes are derivatives of benzene.

Discussion.

Referring to Professor Tilden's statement that it was an objection to Kekulé's formula that benzene did not yield oxalic acid on oxidation, Dr. Japp said that phenol, he believed, gave a considerable quantity of the acid on oxidation with alkaline permanganate.

Mr. Groves added that oxalic acid was obtained in quantity on oxidation of chloranilic acid; and Dr. Perkin remarked that he had obtained a quantity of oxalic acid in preparing picric acid from phenol.

Dr. Perkin said that the magnetic rotatory power of American turpentine was remarkably low, which was a probable indication of the non-existence of a C_6 nucleus.

Dr. Armstrong expressed the opinion that the evidence at disposal was entirely insufficient to enable us to determine the constitution of the terpenes with any degree of probability. He could not accept Dr. Tilden's conclusion that camphene was saturated, as it readily united with a molecular proportion of hydrogen chloride. With regard to the constitution of benzene, his main contention was that the cross connexion of carbon-atoms exhibited in Claus's and similar formulæ was inconceivable; he believed that corresponding carbon-atoms could exercise an influence upon each other although unconnected except indirectly.

Professor Tilden said that his chief object in referring to the constitution of benzene was to emphasise his opinion that whatever the nature of the combination between the carbon-atoms, it did not correspond to that which obtained in ethylene.

73. "Some new compounds of Magnesia with the Halogens: a contribution to the study of the electrolysis of Magnesium Chloride solution." By C. F. Cross and E. J. Bevan.

Their observations on the electrolysis of magnesium chloride in aqueous solution, which is now a process of preparing bleaching solutions on the large scale, had previously made the authors aware that the decomposition was attended by interactions *not* to be explained on the view commonly held, viz., that the ions are magnesium and chlorine, which by secondary interactions give rise to magnesia and hypochlorous acid.

With the view of elucidating the actual mechanism of the electrolysis the authors have studied in the first instance the phenomena at the cathode. The white substance separated under the condition that the solution is not kept in circulation, is not magnesia (hydrate), but a chloroxygen-compound of magnesium, in which the ratio of Cl to

total oxidising power expressed as Cl is approximately 1 : 2. It may be regarded, therefore, as a magnesium hypochlorite. It is worthy of note that the percentage weight of "total oxidising Cl" lies between 30 and 35, calculated on the anhydrous substance. The compounds described were analysed in the freshly prepared and hydrated condition. They differ from the normal magnesium hypochlorite not only in being insoluble, but also in point of their stability.

Similar compounds were obtained on electrolysing solutions of magnesium bromide and magnesium iodide, though in the case of the latter the ratio—Total oxidising iodine : Iodine as silver iodine—is considerably less than 2, viz., approximately 6 : 5. Nevertheless, the compound decomposes ammonia with evolution of nitrogen, and is in all its properties rather a compound than a mixture of iodine with magnesia.

The authors are engaged in studying the phenomena to be observed at the anode during the electrolysis in question, and the composition of the resulting solution in regard to the whole of the chloroxygen-compounds, of which there appear to be at least two.

74. "The Heat of Dissolution of various substances in different liquids." By S. U. Pickering.

The author has explained the constancy of the heat of neutralisation of acids by alkalis on the view that the affinity of the radicles composing the salt molecules concerned is not entirely saturated by their combination, and that the residual affinity of one of these radicles becomes in each case entirely saturated by the solvent. The heat of combination of the atoms, and the heat of dissolution of the molecules which they form, are thus parts of the same operation, and must, therefore, both be chemical in their nature. Dr. Nicol has suggested the possibility of the heat of dissolution of the molecules of four solids showing the relation expressed by $MR_1aq - M'R_1aq = MR'_1aq - M'R'_1aq$, which would render the above-mentioned connexion between the heat of dissolution and formation of the molecules unnecessary. The author shows that if Dr. Nicol's suggestion held good a certain relationship would obtain between the heat of dissolution of two pairs of salts in two different liquids. To investigate this he has determined the heat of dissolution of the nitrates and chlorides of calcium and lithium in water and in alcohol, and has found that they give results showing a difference of 4461 cal. where, according to Dr. Nicol's view, there should be no difference at all.

Other salts were also examined and it was found that the heat of dissolution in alcohol was sometimes greater and sometimes less than in water.

According to the author's views the heat of dissolution should be the same whatever the solvent were, provided (1) that the residual affinity of one only of the radicles constituting the dissolved substance be saturated by the solvent, and (2) that the saturation be effected by *free* affinity of the solvent, *i.e.*, that no alteration in the force with which the molecules or atoms of the solvent are united together be involved. The first condition is ensured by taking an elementary substance instead of a salt; and the author has found that the heats of dissolution of iodine and bromine in various liquids give much more nearly identical results than salts do, and that with liquids containing no oxygen the results are identical within experimental error. Oxygenated liquids give higher results, and the presence of sulphur as a constituent element of the solvent has, to a certain extent, the same effect as oxygen. If the second as well as the first above-mentioned conditions could be secured, the results would probably be in all cases identical?

Discussion.

Professor Ramsay said it appeared that the heats of dissolution of iodine in various media might be arranged in two well-defined groups. Might not this be correlated with the fact that iodine dissolves in certain liquids forming a brown solution and in others forming a violet solution; and with the observation recently made by Loeb that iodine existed in these differently coloured solutions in different molecular states.

75. "The Criteria of Plane and Axial Symmetry." By Henry E. Armstrong.

Wislicenus, in his now widely known paper on the space arrangement of the atoms in carbon-compounds, has termed compounds of the form $\begin{matrix} a\,.\,\mathrm{C}\,.\,b \\ \| \\ b\,.\,\mathrm{C}\,.\,a \end{matrix}$ *axially symmetric*, and those of the form $\begin{matrix} a\,.\,\mathrm{C}\,.\,b \\ \| \\ a\,.\,\mathrm{C}\,.\,b \end{matrix}$ *plane symmetric*. In allocating these formulæ, he has argued, in a case such as is afforded by the two tolane dichlorides, for example, that the compound of higher melting point (143°) is necessarily the plane symmetric modification, as it is produced on chlorinating tolane:

$$\begin{matrix} \mathrm{C_6H_5\,.\,C} \\ \mathrm{C_6H_5\,.\,\ddot{C}} \end{matrix} + \mathrm{Cl_2} = \begin{matrix} \mathrm{C_6H_3\,.\,C\ Cl} \\ \mathrm{C_6H_3\,.\,\dot{C}\ Cl} \end{matrix};$$

and he urges that this conclusion derives support from the behaviour of tolane tetrachloride on reduction. Of the three possible configurations which this compound may acquire, viz.:—

$$\begin{array}{lll} \dot{C}.C_6H_5\ Cl\ Cl & \dot{C}.C_6H_5\ Cl\ Cl & \dot{C}\ C_6H_5\ Cl\ Cl \\ \dot{C}.Cl\ C_6H_5\ Cl & \dot{C}.Cl\ Cl\ C_6H_5 & \dot{C}\ C_6H_5\ Cl\ Cl \end{array};$$

he regards the first and second as far the most likely to exist, especially at low temperatures; both would furnish, on withdrawal of two corresponding chlorine-atoms, the same axially symmetric tolane dichloride, and it is therefore to be supposed that the modification formed in larger quantity on reducing the tetrachloride would be this modification. According to the recent experiments of Blank (*Annalen*, **248**, 1), the two isomeric dichlorides are obtained nearly in the proportion of two parts of that of lower melting point (63°) to one of that of higher melting point; and the axially symmetric structure is therefore, it would seem, as a matter of course, assigned by him to the compound of lower melting point.

The first argument is only valid provided that at the moment of change no isomeric change supervenes, and must be accepted with reserve—if not regarded as altogether untrustworthy—as further study of the changes involved in the production of isomeric compounds appears to make it more and more probable that the final product is very frequently the product of an unperceived isomeric change (cf. these Proceedings, 1887, Abstr. Nos. 99—101; 1888, Abstr. Nos. 50, 51).

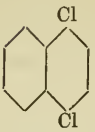
The second is not an argument based on clearly ascertained facts, but derives its force entirely from hypothetical views as to the relative affinities of the radicles present in a compound, and the effect on the ultimate configuration which these affinities would have, and is especially based on the conventional assumption that dissimilar radicles would tend to influence and attract each other more than would similar radicles. But it is to be remembered that we have little certain knowledge of the relative affinities of different radicles, especially of similar as compared with those of dissimilar radicles; indeed, that our views are not based on the study of the radicles themselves, but are mere inferences from the apparent behaviour of the radicles in their compounds. Moreover Thomsen's observations on the heats of combustion of chlorine compounds may be held to some extent to favour a view contrary to that put forward by Wislicenus (cf. *Phil. Mag.*, 1887 [5], **23**, 106).

The most important argument averse to the interpretation given by Wislicenus, however, is to be found in the fact that in cases in which the constitution may fairly be regarded as established, the relation between configuration and physical properties is of the obverse order to that indicated by Wislicenus. Thus, in the case of benzene di-derivatives, the symmetric or para-derivative has always the highest melting point; the same appears to be true of the symmetric tri- and tetra-derivatives; and in the case of naphthalene, in a series

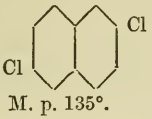
of isomeric di-derivatives, the axially symmetric modification is always that of highest melting point, thus—

M. p. 107°.

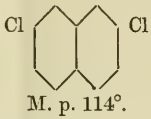
M. p. 83°.



M. p. 68°.



M. p. 135°.



M. p. 114°.

Again, of the four known naphthalenedisulphonic chlorides, the axially symmetric $\alpha'\alpha^{4'}$ modification melts at 183°, the dissymmetric $\alpha\beta$ modification at 128°, the axially symmetric $\beta^2\beta^{3'}$ modification at 226°, and the plane symmetric $\beta^2\beta^{2'}$ modification at 160°.

Employing the argument from analogy, it is therefore probable that the tolane dichloride melting at 143° is the axially symmetric, and that melting at 63° the plane symmetric modification, and also, for example, that elaidic acid—and not oleic acid as Wislicenus assumes—has the "axial" structure. In the case of maleic and fumaric acids the argument here relied on would support the conclusion already arrived at by Van't Hoff and accepted by Wislicenus, which, however, is based not on geometric considerations, but on the observed property of maleic acid to form an anhydride.

It is a noteworthy fact that the majority of "alloisomerides"—to use a term which is sufficiently expressive while it does not beg the question as to the determining cause of the isomerism—are compounds containing unsaturated carbon, usually in association with one of the halogens or oxygen. It does not appear that this circumstance has yet been taken into account, or that the extent to which the peculiarities manifested by the negative elements are concerned in and may condition the isomerism has been in the least considered. The symbolic system introduced by Van't Hoff and adopted by Wislicenus tends to withdraw attention from the consideration of the possible effect of the peculiarities referred to, inasmuch as a "double bond" is represented as the precise equivalent of two, and a treble bond as that of three single bonds; which all observations show is a misrepresentation of the facts.

76. "Derivatives of Methylindole." By H. G. Colman, Ph.D., B.Sc.

By the action of sodium hypobromite solution on methylindole or

methylindolecarboxylic acid, Fischer and Hess (*Ber.*, **22**, 561) obtained a brominated compound which, on treatment with alkali, yielded methylpseudisatin.

It is shown that the brominated substance is dibromomethyloxindole, a white crystalline substance melting with decomposition at 204°.

If sodium hypochlorite be substituted for sodium hypobromite, the corresponding dichloromethyloxindole is obtained, m. p. 145—147°. Both compounds on boiling with alkali, or better with water, yield methylpseudisatin. The phenylhydrazone and oxime of the latter have been prepared: they are yellow, crystalline compounds melting at 145—146° and 180—183° respectively.

By the reduction of dibromethyloxindole in acid solution, monobromomethyloxindole and methyloxindole are successively obtained. Both are white, crystalline compounds, the former melting at 132—134°, and the latter at 86—88°.

Methylpseudisatin, on reduction in acid or alkaline solution, yields methyldioxindole; this crystallises from benzene in needles or prisms melting at 149—151°.

77. "Acetamide and Phenanthraquinone." By Arthur T. Mason, Ph.D., F.I.C.

The author finds that when oximide is heated in sealed tubes with glacial acetic acid at 220—230° C., acetamide is formed, which, however, on recrystallisation from ether or benzene, totally loses the peculiar smell of mice excrement which has hitherto been supposed to be its principal characteristic. Ordinary acetamide, prepared by the distillation of ammonium acetate, also becomes odourless by twice rectifying and rejecting the first portions of the distillate.

Acetamide, when heated with phenanthraquinone in sealed tubes at 220—230° C., using glacial acetic acid as solvent, yields diphenanthrapiazine, an indifferent body, having a melting point over 400° C. and belonging to the "azine" group.

78. "The Action of Ethylenediamine on Succinic Acid." By Arthur T. Mason, Ph.D., F.I.C.

The addition compound, $C_2H_4(COOH)_2 \cdot C_2H_4(NH_2)_2$, is first produced; it crystallises in thick, white prisms melting at 181—182°; if it be heated above this temperature, it parts with water, ethylenedisuccinimide, $\begin{matrix}CH_2 \cdot CO \\ CH_2 \cdot CO\end{matrix}\!\!>\!N \cdot CH_2 \cdot CH_2 \cdot N\!<\!\!\begin{matrix}CO \cdot CH_2 \\ CO \cdot CH_2\end{matrix}$, being formed which melts at 250—251°, and distils undecomposed at 395°. This compound gives the pyrrole reaction on distillation with zinc-dust

containing hydroxide. It is not attacked by bromine and water at 120°, but at 180° ethylenediamine bromhydride is formed. Ethylene disuccinamic acid, $COOH{\cdot}C_2H_4{\cdot}CO{\cdot}NH{\cdot}C_2H_4{\cdot}NH{\cdot}CO{\cdot}C_2H_4{\cdot}COOH$, is prepared from the diimide by boiling with baryta-water; the acid crystallises from water in large, colourless, quadratic plates melting at 184—185°; its silver salt is anhydrous; the calcium salt has the formula $C_{10}H_{14}N_2O_6Ca + 3H_2O$.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Geological and Natural History Survey of Canada. Annual Report. New Series. Vol. II. 1886. Montreal 1887.
From the Survey.

Verhandlungen der Kaiserlichen Leopoldinisch-Carolinischen Deutschen Akademie der Naturforscher. Bände 49–51. Halle 1887.
From the Academy.

Proceedings and Transactions of the Royal Society of Canada for 1887. Vol. V. Montreal 1888. From the Society.

An Introduction to the Study of Meteorites. By L. Fletcher. London 1888. From the Trustees of the British Museum.

Army Medical Department. Report for the Year 1886. London 1888. From the War Office.

Royal College of Surgeons, Ireland. The Carmichael Prize for 1887, "The Medical Profession in the Three Kingdoms in 1887," by T. Laffan. Dublin 1888. From the Council of the College.

Collection des anciens alchimistes grecs, par M. Berthelot et C. E. Ruelle. Seconde livraison comprenant les œuvres de Zosime; texte grec et traduction française. Second Livraison. Paris 1888.
From the Authors.

Laboratory Manual of General Chemistry, by R. P. Williams. Boston 1888. From Messrs. Trübner.

Manganese Steel, by R. A. Hadfield. London 1888.
From the Author.

Smithsonian Miscellaneous Collections. Vols. 32 and 33. Washington 1888. From the Smithsonian Institution.

The Life of Sir William Siemens, by W. Pole. London 1888.
From the Executors.

II. *By Purchase.*

Universal-Pharmakopöe; eine vergleichende Zusammenstellung

der zur Zeit in Europa und Nordamerika gültigen Pharmakopöen, von B. Hirsch. Zweite Auflage, Erster Band. Göttingen 1888.

Untersuchungen aus der Praxis der Gärungsindustrie, von E. C. Hansen. Heft I. München und Leipzig 1888.

L'Art de l'Essayeur, par A. Riche, avec la collaboration de E. Gélis. Paris 1888.

Die Anilinfarben und ihre Fabrikation, von K. Heumann. Erster Theil, Triphenylmethan-Farbstoffe. Braunschweig 1888.

Analyse chimiques des substances commerciales minérales et organiques, par R. Jagnaux. Paris 1888.

Recherches sur les eaux minérales des Pyrénées, par E. Filhol. Paris 1888.

Fortschritte der Theerfarbenfabrikation und verwandter Industriezweige 1877–1887. An der Hand der Deutschen Reichs-Patente dargestellt, von P. Friedländer. Berlin 1888.

Recherches sur les modifications de l'atmosphère, par J. A. De Luc. 2 tomes, 4to. Genève 1772.

Meletemata Philosophica, Adriani Heerebord. 4to. Lugduni-batavorum 1659.

Johannis Beguini Tyrocynium Chimicum, edente Gerardo Blasio. Amstelodami 1669.

De Coloribus Libellus a Simone Portio. 4to. Florentiae 1548.

Onomastikon, seu Lexicon Medicinae Simplicis Othonis Brunfelsii (small folio) 1543.

Ordo Institutionum Physicarum, T. Rutherforth. 4to. Cantabrigiæ 1743.

Jacobi Bruckeri Institutiones Historiae Philosophicae. Lipsiae 1756.

At the next meeting on November 15th, there will be a ballot for the election of Fellows, and the following papers will be read:—

"The principles of Thermochemistry." By S. U. Pickering.

"Note on the mixture of Propyl alcohol and water." By Professors Ramsay and Young.

"Note on the action of Nitric acid on Ammonium chloride." By Dr. Matthews.

"Ethylic cinnamyldiethacetate." By the same.

"Piazine-derivatives." By Dr. Mason.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 58. Session 1888–89.

November 15th, 1888. Mr. W. Crookes, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. Carl Duisberg, Ph.D., Farbenfabriken, vormals Bayer und Co., Elberfeld; Lionel Remond Lenox, Ph.D., Lehigh University, South Bethlehem, Pennsylvania; George Lloyd, 25, Kensington Gardens, Balsall Heath, Birmingham; James Muir, Staunton Harold, Branksome Park, Bournemouth; Robert Hodgson Parker, 26, Harford Street, Norwich; John Percival, B.A., 58, Harwood Road, Walham Green, S.W.; Percy Andrew Ellis Richards, 44, Sinclair Road, Kensington; Emanuel Roberts, Moratna, Ceylon.

The following were duly elected Fellows of the Society:—Messrs. Walter Bromley Cooley, John Burke Fairley, Walter M. Gardner, Archibald Carlyle Mounsey Ingram, Frank Pullinger, A. Alexander Ramsay, Clement J. Rhodes, C. Heinrich Trinks.

The following papers were read:—

79. "The Principles of Thermochemistry." By S. U. Pickering.

The author rejects the thermochemical principles enunciated by Thomsen, Naumann and Berthelot, not only on special grounds, but on the more general ground that they depend on an impossible distinction between chemical and physical actions. A satisfactory explanation of all known thermochemical facts is derived from the recognition of the laws of dissociation and the hydrate theory of dissolution. Every act of combination must be accompanied by the evolution of heat, and in interactions where heat is absorbed this absorption must be due to the fact that one or more of the agents being partially dissociated at the temperature of the interaction, the removal

of one of the products of the dissociation necessitates a further decomposition of the agent. The heat evolved must also be a direct measure of the affinities saturated, and of two possible interactions that which evolves more heat must occur to the exclusion of the other.

The cases of endothermic changes which present difficulties are those in which liquids and solids are concerned. The heat absorbed when many solids are dissolved in liquids cannot be explained by the fusion, but only by the volatilisation of the solid. A mass of water contains some fundamental molecules possessing an energy of 10,000 cal. greater than the average molecular aggregates constituting the mass. These can therefore combine with the salt, and effect its volatilisation with an evolution of heat, even if the heat of volatilisation be nearly 10,000 cal.; other water aggregates then dissociate to supply the place of the free molecules thus removed from the sphere of action.

From theoretical considerations the author arrives at the conclusion that Berthollet's theory as to the division of a base between two acids is correct—that two acids present in equivalent proportions should divide the base equally between them; that, since sulphuric acid acts as a monacid in this respect, H_2SO_4 should be compared with HCl and not with 2HCl; and that, if one of the two acids form a dissociable salt, it would take none or very nearly none of the base. The facts observed, the author argues, are in accordance with these conclusions, and are entirely opposed to the existence of the so-called "avidity" or "affinity" constants advocated by Ostwald and others.

The reason why sulphuric acid acts as a monacid in this respect, or, in other words, why H_2SO_4 and K_2SO_4 interact to form $2HKSO_4$ in spite of the absorption of heat accompanying the action, is that lower hydrates (especially of the acid) are present, and that with these lower hydrates the interaction is exothermic, and, therefore, necessarily occurs, the absorption of heat noticed being due to the dissociation of the higher hydrates to supply the place of the lower ones thus removed from the sphere of action.

Discussion.

Professor Ramsay said that it was merely a matter of nomenclature to distinguish physical attraction, in which each molecule present attracted every other molecule according to some law comparable with the law of gravitation, from chemical attraction, in which selective attraction is exercised; but that he preferred to draw the distinction, where possible, in order to save confusion, though it might be difficult in some cases to do so. He did not believe in the universal presence of complex molecules in liquids and solids: nor did he exclude the

existence of such; the researches of Professor Young and himself, he thought, conclusively established the absence of a complex molecular structure in such liquids as ethyl alcohol and ether; while on the other hand Henry's arguments testified to the complexity of the molecules of certain oxides such as silica. And with regard to water, which specially formed the subject of Mr. Pickering's remarks, while the vapour-density pointed to molecular simplicity, other arguments drawn from its behaviour when examined by Raoult's method were in favour of moderate molecular complexity.

Dr. Armstrong said that he agreed with Mr. Pickering, and thought that it would be necessary in the future to attach a far wider significance to the term chemical action, and to greatly restrict the use of the term physical action—that, in fact, very many so-called physical changes would be found to involve a change in molecular composition or configuration. It was conceivable that in certain cases such as Professor Ramsay had mentioned molecule acted upon molecule chemically, but in such manner that the molecular aggregate was of the dimensions of the mass. By taking into account the action of water, Mr. Pickering had advanced what appeared to be a rational explanation of many facts which hitherto had appeared paradoxical.

Mr. Pickering, in reply to Professor Ramsay, said that the fact that gaseous water was of normal density appeared to him compatible with the existence of complex water molecules: probably a sudden change attended liquefaction or gasification. This argument might be of general application.

80. "Note on the mixture of Propyl Alcohol and Water." By Professor Ramsay, F.R.S., and Professor Young.

Chancel has called attention to the fact that a mixture of propyl alcohol and water in the proportions C_3H_8O : H_2O distils over to the last drop at 87·5° (press. = 738 mm.). Konowalow, however, determined the vapour-pressure of mixtures of the alcohol and water and arrived at results adverse to the conclusion that a definite hydrate exists, and the authors are of similar opinion. They found that the vapour-pressures of the mixture determined by the statical method were uniformly higher than those determined by the dynamical, but the difference is very small and far less than is observed with most dissociating substances, the behaviour being more nearly that of an imperfectly purified stable substance. The results of vapour-density determinations seemed to point to a rise of density with fall of temperature and increase of pressure, but it was afterwards found that the greater part of the rise was due to condensation, probably of water, on the side of the tube. A percentage contraction of 1·85 was

observed on mixing the alcohol with water —71·46 per cent. alcohol to 28·54 per cent. water. The composition of the mixture of constant boiling point was found to vary with the pressure under which it was distilled.

Discussion.

Mr. Howard expressed the opinion that propyl alcohol and water formed a definite compound until vaporised; the behaviour of the various lower alcohols with water, and the fact that the solubility of amyl alcohol in water diminished as the temperature rose, all tended to prove that the alcohols formed hydrates.

Professor Young, in support of the opinion that the mixture was not a hydrate, recapitulated the arguments which he and Professor Ramsay had advanced in previous papers in discussing the properties of various liquids and liquid mixtures.

81. "Note on the Action of Nitric Acid on Ammonium Chloride." By F. G. Mathews, Ph.D.

The principal gaseous product of the action of nitric acid on ammonium chloride in solution is nitrous oxide, and not nitrogen, as has been previously stated; the gas is mixed with small quantities of chlorine and oxychloride of nitrogen, from which it may be freed by washing with sodium hydroxide. The nitrogen of the nitric acid as well as of the ammonium chloride is concerned in the formation of the nitrous oxide. The interaction is of general application, and takes place in all cases in which a solution of an ammonium salt is heated in the presence of nitric acid and hydrogen chloride.

82. "Ethylic Cinnamyldiethacetate." By F. G. Mathews, Ph.D.

A simpler method of preparing ethylic cinnamyldiethacetate than has been previously known is to allow a mixture in molecular proportions of benzaldehyde and ethylic diethacetoacetate saturated with hydrogen chloride to stand for about a month: the product separates slowly in crystals which are practically pure ethylic cinnamyldiethacetate. On hydrolysis with barium hydroxide, cinnamic and diethacetic acids are produced, small quantities of a ketone only being formed. An attempt to prepare the corresponding monethyl-derivative in a similar manner failed. On trying to prepare similar derivatives of ethylic mono- and di-methacetoacetate, no products could be isolated. the action appearing to be more complex than in the case of the corresponding ethyl compounds.

83. "The isomeric Sulphonic acids of Betanaphthylamine." By Arthur G. Green.

It is known that on sulphonating betanaphthylamine by means of ordinary sulphuric acid, a mixture of α- and γ-acids is produced at low temperatures, and at higher temperatures (160—170°) a mixture of β and δ: according to the formulæ usually assumed for these acids, the first pair have their sulpho-groups in α-positions, the second pair in β-positions; and their formation is exactly analogous to that of the α- and β-sulphonic acids of naphthalene. According to Dahl, the product at 100° consists of α-, β- and γ-acids, but the author finds that as was to be expected, the δ-acid is also present. The four acids can be readily isolated by a slight modification of Dahl's process. The ammonium salts of the four acids were found to differ in a very characteristic manner: that of the β-acid is less soluble than the three isomeric salts, and by means of this salt, the β-acid was obtained in a pure state, and was found to crystallise in prismatic needles, not in nacreous plates, the formation of which is shown to be dependent on the presence of δ-acid. Although betanaphthylamine gives four isomeric acids on sulphonation, only two sulpho-acids are supposed to be formed by sulphonating betanaphthol; but bearing in mind the analogous behaviour of hydroxy- and amido-compounds, it would appear much more probable that four acids are formed in the latter case also, and hence a search was made for the δ-sulphonic acid in the product of sulphonation of betanaphthol at 100°. As the separation of isomeric betanaphtholsulphonic acids presents great difficulties, the method adopted consisted in converting the sulphonation product into the corresponding betanaphthylaminesulphonic acids and separating these. By this means it was proved that the product formed at 100° is a mixture of the β- and δ-isomers. Hence at higher temperatures at any rate betanaphthol behaves on sulphonation like betanaphthylamine; whether this is the case at low temperatures also remains to be seen.

Discussion.

Mr. Wynne asked whether Mr. Green had any evidence in favour of the formulæ he had adopted for the α (Badische) and γ (Dahl) betanaphthylaminesulphonic acids. The γ-acid was more usually represented by the formula $NH_2 : SO_3H = 2 : 1'$. With regard to the α or Badische acid, it was to be noted that Cleve had assigned the constitution adopted by Mr. Green to the dichloronaphthalene melting at 34°; that Forsling had assigned the constitution 1 : 3 or 1 : 2 to the dichloronaphthalene melting at 61·5,° obtainable from the Badische acids; and that Erdmann and Kirchhoff had obtained a dichloro-

naphthalene melting at 61·5° which was unquestionably heteronucleal. At present, therefore, Mr. Green's formula for the betanaphthylamine-α-sulphonic acid could not be accepted.

Looking at the variation in the proportions of the four betanaphthylaminesulphonic acids formed on sulphonating at different temperatures, Mr. Wynne suggested that the conversion of the α- and γ-acids into the β- and δ-acids at 160° might be explained by supposing that in the presence of the sulphuric acid the α-acid was converted exclusively into the β-acid, and that the γ-acid underwent a similar change into the δ-acid, which itself at higher temperatures (or by a prolonged action of the sulphuric acid at 160°) would undergo conversion into the β-acid. Such a change, though perhaps different in its course, would be analogous in result to that described by Professor Armstrong and himself in the case of the monosulphonic acids of the β-halogen-derivatives of naphthalene having a constitution similar to that of the Badische acid.

Dr. Armstrong referred to Emmert's observation that the betanaphthol-α-sulphonic acid corresponding to betanaphthylamine-α-sulphonic acid is convertible into a dihydroxynaphthalene different from hydrobetanaphthaquinone, as incompatible with the conclusion that the α-acid was the 1 : 2 compound; moreover, an acid in which the SO_3H and OH groups were in the relative positions 1 : 2 would not, he thought, be capable of forming azo-colours. He then pointed out that the conclusions at which Mr. Wynne and he had arrived concerning the constitution of the dichloronaphthalene obtainable from the Badische acid were irreconcilable with Mr. Green's formula (cf. the following Abstract).

Mr. Green, in reply, defended the view that the α-acid was the ortho-compound mainly on the ground that it and the corresponding hydroxy-acid differed so greatly in properties from their isomers.

84. "The constitution of the Dichloronaphthalenes, especially the $\alpha\beta$-compounds." By Henry E. Armstrong and W. P. Wynne.

The three possible $\alpha\alpha$- and the two possible heteronucleal $\beta\beta$-dichloronaphthalenes are all known, and not only are they known, but there can be little doubt that the formulæ now ascribed to the several modifications (comp. Abstracts of Proceedings, 1888, p. 95) are correct expressions of their constitution.

The object of the present note is to point out that the four possible $\alpha\beta$-dichloronaphthalenes are also known, and to draw attention to the explanation of the somewhat discrepant statements on record relating to the so-called θ-modification, melting at about 61°. This was first prepared by Cleve, who obtained it from one of the three α-nitro-acids formed on nitrating naphthalene-β-sulphonic acid; he subsequently

obtained a dichloronaphthalene having the same melting point from a second of these three acids, but left it an open question whether two isomers of the same melting point existed, or whether an isomeric change took place on treating the nitrosulphochloride with phosphorus pentachloride. Dichloronaphthalene melting at about 61° has since been prepared (1) by Arnell from β-chloronaphthalenesulphonic acid; (2) by Cleve from dichloralphanaphthylamine; (3) by Claus from betanaphthol-α-sulphonic acid (Bayer's modification); (4) by Forsling from betanaphthylamine-α-sulphonic acid (the Badische acid); (5) by Erdmann and Kirchhoff from parachlorophenylparaconic acid. Forsling has quite recently stated (*Berichte*, 1888, 2802) that the modification melting at about 61° is either 1 : 2 or 1 : 3 dichloronaphthalene, his conclusion being doubtless based on Cleve's statement that dichloralphanaphthylamine yields phthalic acid on oxidation, and is therefore to be regarded as homonucleal. Now the authors have found (*British Association Report*, 1887, p. 231) that two distinct dichloronaphthalenes have been regarded as one, and that while that from dichloralphanaphthylamine melts at 61·5°, that from Arnell's β-chloronaphthalenesulphonic acid and from the Badische or betanaphthylamine-α-sulphonic acid melts at about 64°; the chloride of the acid obtained on sulphonating the former melts at about 148°, the isomeric sulphochloride obtained from the latter melting at 119°. In support of Cleve's statement that dichloralphanaphthylamine is a homonucleal compound, they are able to state that it yields the same trichloronaphthalene (m. p. 92°) as dichloralphanaphthol, an undoubted homonucleal derivative. The dichloronaphthalene melting at 61·5° is, therefore, either the 1 : 2 or the 1 : 3 homonucleal modification. That melting at 64° must be regarded as the 1 : 2′ or 1 : 3′ heteronucleal modification, inasmuch as the dichloronaphthalene melting at 34° discovered by Cleve in 1887 is also a homonucleal compound.

The dichloronaphthalene melting at 34° was obtained by Cleve from chlorobetanaphthylamine and from chlorobetanaphthol; it may also be prepared from the chloralphanaphthylamine which Cleve obtained by reducing dichloralphanaphthylamine. Cleve's statement that chlorobetanaphthylamine is a homonucleal compound, since it yields phthalic acid on oxidation, is confirmed by the observation that a sulphonic acid may be prepared from chlorobetanaphthol, which is converted on treatment with bromine into a bromhydroxyquinonesulphonate, identical with that which may be obtained from Schaefer's betanaphtholsulphonic acid, in which the bromine is undoubtedly present in the quinone nucleus.

The fourth αβ and the second heteronucleal dichloronaphthalene is the η-modification, melting at 48°. This was originally obtained by Cleve from one of the three α-nitro-derivatives of naphthalene-β-

sulphonic acid; it has since been prepared by Forsling from beta-naphthylamine-γ-sulphonic acid (Dahl's modification), and synthetically by Erdmann and Kirchhoff. The authors have recently obtained it by distilling their ? β-naphthalenedisulphonic acid (Abstracts of Proceedings, 1886, p. 231) with phosphorus pentachloride; attention is to be called to the fact that this had previously been stated to be a method of preparing the θ-modification, melting at 61·5° (*Brit. Assoc. Report*, 1887, p. 232); how the mistake arose they are unable to explain, but a mistake was undoubtedly made, as a portion of the original specimen of the sulphochloride, melting at 150°, referred to in the British Association Report, gave on hydrolysis η- and not θ-dichloronaphthalene. The sulphochlorides prepared from the two dichloronaphthalenes melting at about 48° and 61° respectively have the same melting point, and hence the mistake was overlooked until recently, when a large quantity of disulphonic acid was prepared and converted into dichloronaphthalene.

It being determined that the two modifications melting at 34° and 61·5° are the two possible homonucleal $\alpha\beta$-dichloronaphthalenes, it remains only to ascertain which is the 1 : 2 and which is the 1 : 3 compound; the authors have succeeded in solving this problem somewhat unexpectedly by studying so-called α-dichloronaphthalene, m. p. 38°, which is obtained on heating naphthalene tetrachloride with alcoholic potash. On sulphonating this compound, two isomeric sulphonic acids are formed, the chlorides of which melt at 133° and 148°, but as these are the melting points of the chlorides formed from the acids which result on sulphonating β-dichloronaphthalene (m. p. 68°) and θ-dichloronaphthalene (m. p. 61·5°) respectively, the two sulphochlorides from α-dichloronaphthalene were hydrolysed; *that melting at* 148° *gave* θ-, *and that melting at* 133° β-*dichloronaphthalene*, proving the supposed uniform α-dichloronaphthalene to be a mixture of θ and β. From this it follows, as only a single $\alpha\beta$ homonucleal dichloronaphthalene can be obtained from naphthalene tetrachloride, viz., the 1 : 3 modification, that θ-dichloronaphthalene melting at 61·5° is the 1 : 3 derivative, and that melting at 34° must be regarded as the 1 : 2 derivative. This conclusion is supported by Widman's observation (*Bull. Soc. Chim.*, **28**, 506; *Ber.*, 1882, 2160) that α-dichloronaphthalene yields two tetrachlorides—one an oil yielding γ-tetrachloronaphthalene, the second a crystalline solid melting at 172°, indistinguishable from that obtainable from β-dichloronaphthalene. It is also confirmed by the observation that on hydrolysing the dichloronaphthalenesulphonic acids prepared in accordance with Widman's directions from naphthalene-α- and β-sulphonic chlorides, θ-dichloronaphthalene, melting at 61·5°, is obtained from the α-acid, and β-dichloronaphthalene from the β-acid.

At present the data are not sufficient to determine whether the heteronucleal modification melting at 48° is the 1 : 3 and that melting at 64° the 1 : 2 derivative, or *vice versâ*. Erdmann and Kirchhoff have indeed put forward the view that η-dichloronaphthalene is the 1 : 3 modification, but their method cannot be regarded as trustworthy, as the origin of the hydroxyl in their naphthol derivatives cannot be determined. The authors anticipate that the study of the sulphonic acids of the dichloronaphthalenes, in which they have long been engaged, will lead to results which will permit of the constitution of isomerides such as the η and the isomeric heteronucleal $\alpha\beta$-dichloronaphthalenes being determined beyond question.

85. "Piazine-derivatives." By Dr. Arthur T. Mason.

In this paper, which is an account of a continuation of work described in the *Berichte*, **20**, 267, the author adopts Widman's nomenclature (*J. pr. Chem.*, **38**, 135) : the "Ketines" (V. Meyer), "Pyrazines" (Wolff, Mason), "Aldines" (V. Meyer), and all compounds containing a ring of four carbon-atoms and two nitrogen-atoms in para-position are now termed *Paradiazines*, or *Piazines*.

The author finds that the condensation product obtained from phenanthraquinone and ethylenediamine is not a dihydride as formerly stated, but the base *phenanthrapiazine*.

Diphenylpiazinedihydride, prepared from benzil and ethylenediamine, which is very unstable towards acids, gives on distillation a very stable base (2, 3) *diphenylpiazine;* this crystallises from 50 per cent. alcohol in large colourless plates, melting at 118—119°; it is only a weak base. The chloroplatinate, $C_{16}H_{12}N_2,PtCl_6$, forms long, yellow, prismatic needles.

By the action of sodium on a solution of 2, 3 diphenylpiazine in amyl alcohol, two hydrides were obtained of the formula $C_{16}H_{18}N_2$. α (2, 3) *Diphenylpiazinehexhydride* crystallises from light petroleum in long, slender, white needles, melting at 122—123°, and possesses strong basic properties. The *hydrochloride*, $C_{16}H_{18}N_2{\cdot}2HCl$, forms long, glistening, white needles, melting at 310°. The *chloroplatinate*, $C_{16}H_{18}N_2H_2PtCl_6 + \frac{1}{2}H_2O$, forms golden-yellow prismatic needles. The *nitroso-derivative*, $C_{16}H_{16}N_6O_4$, crystallises in white prismatic needles melting at 142—143°. Methyl iodide gives with the α-hydride the *hydriodide of* (1, 4) *dimethyl* (2, 3) *diphenylpiazine tetrahydride*, $C_{18}H_{22}N_2HI$, which forms long colourless needles; the base of this salt crystallises from hot water in long colourless needles melting at 263—264°; the *chloroplatinate*, $(C_{18}H_{22}N_2)_3{\cdot}2HCl(PtCl_4)_2 + 8H_2O$, forms yellow prismatic needles. β (2, 3) *Diphenylpiazinehexahydride*, which is found in the mother-liquors from

which the α-compound has separated, together with a third basic hydride, crystallises from 50 per cent. alcohol in long, silky, white needles, which on drying become dull white. It melts at 108—109°, and has strong basic properties. The *hydrochloride*, $C_{16}H_{18}N_2 2HCl$, forms colourless prismatic needles, melting at 295°. The *chloroplatinate*, $C_{16}H_{18}N_2 \cdot 2HClPtCl_4 + 2H_2O$, forms long light yellow needles. On oxidation (2, 3) diphenylpiazine yields a *phenylpiazinecarboxylic acid*, melting at about 202°, which yields well-characterised salts.

The author, in conjunction with Mr. L. A. Dryfoos, is extending the research to the α-diketones of the fatty series.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

An Introduction to the Science and Practice of Photography, by Chapman Jones. London 1888. From the Author.

Praktische Metallurgie, von A. A. Schünemann. Quedlingburg and Leipzig 1839. From B. H. Brough.

New experiments and observations made upon the Icy Noctiluca, by R. Boyle. London 1681–2. From B. H. Brough.

At the next meeting, on December 6th, there will be a ballot for the election of Fellows, and the following papers will be read:—

"A method of determining Vapour-densities applicable at all temperatures and pressures." By Dr. W. Bott.

"Derivatives and some new Colouring Matters obtained from α-Pyrocresol." By Dr. W. Bott and J. Bruce Miller.

"The action of Ammonia on Tungsten Oxychlorides." By Dr. S. Rideal.

HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY, ST. MARTIN'S LANE.

ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 59. Session 1888–89.

December 6th, 1888. Mr. W. Crookes, F.R.S., President, in the Chair.

Messrs. Lewis Edmunds, J. B. Readman and J. Cowper were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Charles Lightfoot Barnes, The Steps, Bromsgrove, Worcester; Albert Cooper, Grimstone Lawn, Haven Green, Ealing; William Hepworth Dixon, Heatherdale, Woodford Green, Essex; B. S. Gott, B.A., Wesley College, Sheffield; Frederick Charles Garrett, B.Sc., 4, Kempson Road, Walham Green, S.W.; Robert J. Gow, Halebank Terrace, Ditton, Widnes; Edward Gudeman, Ph.B., P.O. Box 3001, New York City; Allan Twistleton Hall, Inglebank, Newlands, Hull; John A. Hall, 126, Lloyd Street, Greenhays, Manchester; Cecil Leigh, c/o A. H. Allen, 67, Surrey Street, Sheffield; Arthur Lloyd MacLeroy, M.A., 12, George Street, Bathwick Hill, Bath; Frank K. Peace, Monton Grange, Eccles, near Manchester; Charles W. Priestley, B.Sc., Abbey House School, Tewkesbury; John Provis, Poldice House, North Adelaide, South Australia; Edgar Richards, Office of Internal Revenue, Washington, D.C.; Siegfried Ruhemann, Ph.D., M.A., University, Cambridge; Walter Venis, Benares, India.

The following were elected Fellows of the Society:—Messrs. Charles M. Adams, John Hope Belcher, B.A., William Berry, William Dunsmore Bohm, Frank Bower, James Edward Brunker, George Alexander Byrn, John Morrow Campbell, Vaughan Cornish, B.Sc., William Douglas, Arthur George Everard, Henry Forth, Frederick Bickell Guthrie, John Hansfield, Urban Arthur Jackson, Alfred Battye Knapps, Oscar Lowman, B.A., Ph.D., William Marshall, George Edward Perry, Hubert N. B. Richardson, John S. Rigby, John Sanderson, Thomas Oliver Sandolt, William Jay Schieffelin, Arthur Landauer Stern, William Taylor, Charles Turner, John Laurence Van-Geyzel, I. T. Ainslie Walker, Edward Dalrymple

Walrond, B.A., Frederick W. Warrick, Edward J. Way, Ernest W. Whieldon, R. W. Woosnam.

The following papers were read :—

86. "A Method of determining Vapour-density, applicable at all Temperatures and Pressures." By William Bott, Ph.D., Berkeley Fellow of Owens College.

The apparatus consists of a large Victor Meyer's bulb, carrying a detachable head-piece, which can be connected with the air-pump. The neck of the bulb communicates with a mercury pressure-gauge, which again is connected with a wide measuring tube attached to an adjustable mercury reservoir. The experiment is conducted as follows. The substance having been placed in the head-piece of the vessel, the latter is heated until the volume has become constant. The apparatus is then exhausted as far as may be requisite, and the reservoir so adjusted that the graduated measuring tube is filled with mercury. The pressure indicated by the gauge having been carefully noted, the substance is allowed to drop into the hot part of the vessel, and the surplus pressure produced by its evaporation is removed by drawing off an equivalent volume of air into the measuring tube until the initial pressure in the gauge has been restored. From the volume of gas measured in the graduated tube, the density referred to hydrogen is obtained by the formula—

$$d = 8484893 \frac{S(1 + 0{\cdot}00367t)}{VP}.$$

S = weight of substance; V = volume of gas in measuring tube; P = pressure of gas in measuring tube; t = temperature of gas.

Discussion.

Prof. Ramsay, remarking on a statement made by the author that he proposed to make use of the apparatus in studying the influence of pressure on dissociation, said that recent investigations had shown that the Victor Meyer form of apparatus was by no means a suitable one for the study of such problems; and he expressed the opinion that for this reason results, such as those recently published by Nilson and Pettersson could not be accepted as final.

87. "Some derivatives and new colouring matters of α-Pyrocresole." By William Bott, Ph.D., and J. Bruce Miller.

Trichlor-α-pyrocresole, $C_{15}H_{11}Cl_3O$, produced by direct chlorination of pyrocresole, forms fine, silky needles, soluble in boiling benzene

and chloroform, insoluble in alcohol and ether; it melts at about 225°.

Dinitro-α-pyrocresole oxide, $C_{15}H_{10}(NO_2)_2O_2$, is obtained from α-pyrocresole oxide by careful nitration in the cold and subsequent treatment with alcohol. It forms yellowish-white crystals, sparingly soluble in acetic acid and freely in hot nitrobenzene; it melts at 235°.

Tetramido-α-pyrocresole oxide, $C_{15}H_8(NH_2)_4O_2$, is obtained by reduction in acid solutions from the corresponding tetranitro-derivative; it is a greenish-yellow powder, soluble in acids, and melts above 300°.

Diamido-α-pyrocresole oxide, $C_{15}H_{10}(NH_2)_2O_2$, prepared from dinitro-α-pyrocresole oxide, resembles the tetranitro-derivative in its properties.

Both amido-compounds can be diazotised, and the diazo-salts interact with phenols in alkaline solution. Two oxyazo-compounds have thus been obtained from β-naphthol, representing the first colouring matters prepared from pyrocresole. Both interact with concentrated sulphuric acid in a characteristic manner, their behaviour resembling that of safranine. The colouring matters in the pure state are dark red powders, insoluble in water; they can be converted into soluble sulphonic acids by treatment with fuming sulphuric acid; the solutions dye silk and wool a fine maroon and salmon colour respectively.

By the action of ammonium sulphide on tetranitro-α-pyrocresole oxide in alcoholic solution, a red and a yellow substance have been obtained, which are evidently azo-derivatives, but have not yet been examined more closely. The yellow substance is somewhat soluble in hot water, the solutions dyeing silk a fine yellow shade.

88. "Berberine." By W. H. Perkin, jun.

Several analyses of the base and also of its chlorhydride showed that these substances were not adapted to the purpose on account of their containing water of crystallisation which can only partially be removed by dehydration: a fact which has been previously noticed by other chemists. Berberine appears to crystallise with 5 to $5\frac{1}{2}$ mol. props. of water, 2 of which remain when the substance is dried at 100° till constant. Berberine chlorhydride, dried over sulphuric acid in a vacuum at a temperature of about 40°, has the formula $C_{20}H_{17}NO_4HCl + 2H_2O$. The chloroplatinate, iodhydride and nitrate, however, are well adapted for analytical examination, and the results which they afford agree closely with those required on the assumption that berberine is $C_{20}H_{17}NO_4$.

When oxidised with an excess of potassium permanganate in slightly alkaline solution, berberine yields, as principal product,

hemipinic acid, $C_{10}H_{10}O_6$, as Schmidt and Schilbach (*Arch. Pharm.* [3], 164—170) have already shown. In view of the interesting results lately obtained by Goldschmiedt in his examination of hemipinic and methemipinic acids, the author has carefully re-examined the hemipinic acid from berberine, and is convinced that it is identical with that obtained by the oxidation of narcotine. The acid from berberine contains two (OCH_3) groups; on fusion with potash it yields protocatechuic acid, and on distilling it with ethylamine, hemipinethylimide, melting at 96°, is formed. This latter substance possesses all the properties of the hemipinethylimide obtained by Liebermann by the action of ethyl iodide on the potassium salt of hemipinimide (from narcotine), and thus the identity of the two hemipinic acids from berberine and narcotine is proved.

Besides hemipinic acid, small quantities of at least two other acids are formed by the oxidation of berberine; one of these melts at 238—242°, and appears to be identical with berberonic acid (or carbocinchomeronic acid?).

If berberine is carefully oxidised with a limited quantity of permanganate, a number of new substances are formed, three of which have already been obtained in a state of purity: a new acid, $C_{20}H_{17}NO_9$, which melts at 143°, and two neutral substances, $C_{20}H_{17}NO_8$ and $C_{20}H_{16}NO_7$, all of which yield protocatechuic acid (berberinic acid?) on fusion with potash. The compound $C_{20}H_{17}NO_8$ melts at 236°; it is insoluble in cold solutions of alkaline carbonates, but dissolves in potash, ammonia, &c., forming well-defined salts. The silver salt appears to have the formula $C_{20}H_{15}NO_8Ag_2 + 4H_2O$.

The compound $C_{20}H_{15}NO_7$ (?) melts at 150°, and is insoluble in alkalis.

When heated with a fuming aqueous solution of hydrogen iodide, berberine yields methyl iodide and a phenolic substance which from the analysis of its sulphate appears to have the formula $C_{18}H_{13}NO_4$, being derived from berberine by the displacement of two methyl-gronps. Several determinations of the number of (OCH_3) groups by Zeisel's method have shown that there are two such groups present in the berberine molecule.

The author has also examined berberinic acid—one of the acids obtained by Hlasiwetz and Gilm (*Jahresbericht*, 1864, 407), by fusing berberine with potash. This acid is decomposed on distillation into carbon dioxide and homopyrocatechol—a decomposition which proves that the acid must be looked upon as a carboxylic acid of this phenol.

The behaviour of berberine towards methyl and ethyl iodides, benzylchloride, &c., has also been studied; it appears in opposition to the results of Henry (*Annalen*, **115**, 133), that the alkaloïd does not form additive compounds with these substances.

89. "The action of Ammonia on some Tungsten compounds." By Dr. S. Rideal, D.Sc.

Wöhler in 1858 found that a compound containing nitrogen, hydrogen and oxygen was obtained by the action of ammonia on heated tungstic oxide, and also a compound containing nitrogen and hydrogen from ammonia and tungsten chloride; analyses of different specimens, however, gave varying results.

According to the author's experiments, ammonia effects the removal of a part only of the oxygen in tungstic oxide, and the black products vary greatly in composition, the average of many analyses agreeing best with the formula $W_5N_6H_3O_5$. When tungstic oxide is heated with ammonium chloride, a similar black product is obtained. The amount of tungsten in different specimens varies between 83·9 and 81·0 per cent., the amount of nitrogen being less than in the compounds formed by means of ammonia; the mean composition of the products in this case may be represented by the formula $WN_2{\cdot}WO_3$.

Ammonia acts on the yellow tungsten oxydichloride in the cold, forming ammonium chloride and a dark-brown product which contains no nitrogen and appears to consist of the dioxide WO_2; this interaction is similar to that of ammonia and chromyl dichloride.

Ammonia also acts on the red tungsten oxytetrachloride, forming a black compound; this contained 88·9 per cent. of tungsten, but the amount of material was insufficient for a determination of the nitrogen. It seems probable that the product is the same as that found when ammonia acts on the hexachloride; *i.e.*, the nitride W_2N_3.

The action of ammonia on tungsten hexachchloride was studied by Wöhler, who was of opinion that two compounds were formed: viz., $2WN_2 + W(NH_2)_2$ and $2WN + W(NH_2)_2$. This conclusion was based on determinations of tungsten and nitrogen in the samples prepared, but hydrogen was not estimated. The author has re-examined the black powder formed in the interaction in question, and has obtained numbers agreeing with those of Wohler for the tungsten and nitrogen percentages, but he considers that the final product is free from hydrogen and that it is the nitride W_2N_3.

Dry ammonia has no action on finely divided tungsten even at a red heat, and seems also to be without action on the blue oxide.

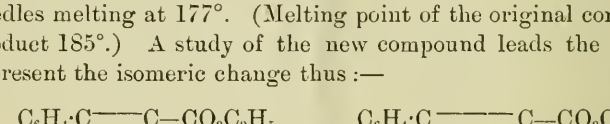
Discussion.

The President drew attention to the anomaly involved in the use of the name *Tungsten* and the symbol W.

90. "Condensations of α-Diketones with Ethylic Acetoacetate." By Francis R. Japp, F.R.S., and Felix Klingemann, Ph.D.

In a paper entitled "Condensations of Glyoxal with Ethylic Malonate and Ethylic Acetoacetate," by Max Polonowsky (*Annalen*, **246**, 1), it is stated, as a reason for undertaking the investigation, that only the condensations of these ethereal salts with *mon*aldehydes and *mon*oketones have hitherto been studied. Polonowsky has evidently overlooked the fact that the condensation of a *di*ketone—phenanthraquinone—with ethylic acetoacetate has been described by Japp and Streatfeild (Trans., 1883, 27). The authors, therefore, wish to point out that they are engaged in investigating the condensation-product, $C_{20}H_{16}O_4$—ethylic phenanthroxylene-acetoacetate—obtained by Japp and Streatfeild. The following interactions have been studied :—

By heating with *formic acid* (sp. gr. 1·22) at 130° the condensation compound is transformed into an isomeride crystallising in short needles melting at 177°. (Melting point of the original condensation-product 185°.) A study of the new compound leads the authors to represent the isomeric change thus :—



The iso-compound would thus contain a closed chain of 5 carbon-atoms. It yields a hydrazone, $C_{20}H_{16}O_3(N_2HC_6H_5)$, melting with decomposition at 210—212° ; whereas phenylhydrazine and the condensation-product do not interact under ordinary conditions. The iso-compound is converted by acetic anhydride into an acetyl-derivative, $C_{20}H_{15}(C_2H_3O)O_4$, which crystallises from benzene in thick needles melting at 165—170°. The iso-compound is converted by hydrolysis with aqueous caustic soda into the corresponding monobasic acid, $C_{18}H_{12}O_4$; this crystallises from alcohol in satiny needles which melt at 267—269° with decomposition. The condensation compound cannot be hydrolysed under these conditions (*vide infra*). With bromine the iso-compound gives a monobromo-derivative, $C_{20}H_{15}BrO_4$, which melts at 217° with decomposition, instead of the expected additive dibromide.

By heating with glacial *acetic acid* at 130—140°, the condensation-product yields a mixture of three compounds ; (1.) A compound of the formula $C_{20}H_{14}O_3$, which crystallises in white silky needles, insoluble in boiling acetic acid, and which decomposes without previous fusion at about 285° ; this is formed with elimination of 1 mol. of water. (2.) The acetyl-derivative, $C_{20}H_{15}(C_2H_3O)O_4$ (m. p. 165—170°), already mentioned as obtained from the iso-compound. This acetyl-derivative gives with phenylhydrazine the same hydrazone, and

with caustic soda the same monobasic acid as the iso-compound, the acetyl-group being in both cases eliminated. (3.) A compound of the formula $C_{40}H_{28}(C_2H_3O)_2O_7$, which crystallises from acetic acid in rectangular plates melting at 227°; this is formed only in small quantity—apparently by elimination of 1 mol. of water from 2 mols. of the acetyl-derivative.

Propionic acid converts the condensation-product into the before-mentioned compound, $C_{20}H_{14}O_3$, together with a propionyl-derivative, $C_{20}H_{15}(C_3H_5O)O_4$, melting at 134°.

By boiling the condensation-product with *sulphuric acid* diluted with twice its weight of water, it is converted quantitatively into the iso-compound $C_{20}H_{16}O_4$, already described as obtained with formic acid (*vide supra*).

By boiling the condensation-product with *alcohol*, to which a few drops of *sulphuric acid* have been added, it is converted into the compound $C_{20}H_{15}(C_2H_5)O_4$, which crystallises from alcohol in rectangular or prismatic crystals melting at 143—144°. But if the condensation-product is heated with a mixture of equal weights of alcohol and sulphuric acid at 100°, it gives a compound, $C_{17}H_{12}O_2$, which crystallises from phenol in microscopic six-sided plates, melting with decomposition at 276—277°; $C_{20}H_{16}O_4 + H_2O = C_{17}H_{12}O_2 + C_2H_5{\cdot}OH + CO_2$.

By warming it with an *alcoholic solution of hydrogen chloride*, the condensation-product is converted into the compound $C_{20}H_{15}ClO_3$, which crystallises from a mixture of benzene and light petroleum in lustrous flat needles melting at 140°.

The condensation-product is hydrolysed by *alcoholic potash* in the cold; heating must be avoided. The resulting acid is unstable, and has not been obtained in a crystallised condition; when freshly precipitated it dissolves in alkaline carbonate, but loses this property on standing. It dissolves in cold alcohol; on heating, the solution deposits the compound $C_{17}H_{12}O_2$, which crystallises from phenol in star-shaped groups of needles, melting with decomposition at 259°; this is isomeric with the compound already described as obtained by heating the condensation-product with a mixture of equal weights of sulphuric acid and alcohol.

The authors have also obtained a condensation compound from benzil and ethylic acetoacetate. It appears to belong to a different class from the phenanthraquinone compound. They also intend to study the condensation of ethylic benzoylacetate with benzil and phenanthraquinone.

91. "Thionyl Thiocyanate." By G. C. McMurtry.

Thionyl thiocyanate, $SO(SCN)_2$, is prepared by the action of

thionyl chloride, dissolved in cold carbon bisulphide, on mercuric thiocyanate. It is an orange-coloured amorphous powder, insoluble in cold water, alcohol, ether, petroleum, phenol, chloroform, amyl alcohol and acetic acid, but readily soluble in carbon bisulphide, and to a less extent in hot benzene.

92. "Mercuric chlorothiocyanate." By G. C. McMurtry.

Mercuric chlorothiocyanate, $ClHg{\cdot}SCN$, or $HgCl_2{\cdot}Hg(CSN)_2$, may be obtained by crystallising mercuric thiocyanate with mercuric chloride. It crystallises in monosymmetric prisms, sparingly soluble in cold water, but readily soluble in hot water and in alcohol.

93. "The Action of Chromium Oxychloride on Pinene." By G. G. Henderson, B.Sc., M.A., and R. W. Smith.

The authors find that pinene and chromium oxychloride interact very readily, forming a solid compound of the formula $C_{10}H_{16}{\cdot}2CrO_2Cl_2$. This is decomposed by water, yielding an oil which may be purified by distillation with steam, and which has a composition expressed by the formula $C_{20}H_{33}OCl$. It is possible that this oil may be a mixture of the two compounds $C_{10}H_{18}O$ and $C_{10}H_{15}Cl$, but the authors were unable to separate it into two portions by steam-distillation; it is not attacked by alcoholic potash, does not combine with bisulphites, is unaffected by acetic chloride, and does not interact with either hydroxylamine or phenylhydrazine. When distilled under diminished pressure it loses the elements of a molecule of water, yielding an oil of the composition corresponding to the formula $C_{20}H_{31}Cl$.

94. "Tectoquinone." By R. Romanis, D.Sc., Rangoon College.

In a former communication (Trans., 1887) the author described a substance found in teak resin (*Tectonia grandis*), and also in the products of the destructive distillation of the wood, having the composition $C_{18}H_{16}O_2$, and the properties of a quinone. It may be separated from the tar by caustic soda, which dissolves the tar, leaving a curdy mass containing the quinone, mixed with a hydrocarbon of the composition C_nH_n, melting at 194°, and other substances. The quinone is separated by dissolution in boiling alcohol of 50 per cent., in which the other substances are insoluble; it separates as the liquid cools in a felted mass of soft woolly crystals; from strong alcohol it is deposited in oblique rhombic prisms of an amber colour, resembling sulphur. It melts at 171°, sublimes slowly at ordinary temperatures, sensibly at 100° C., and rapidly near its melting point. By careful heating between watch-glasses it can be sublimed without decomposition,

condensing in yellow rhombic plates. It is a very stable substance, dissolving in sulphuric and nitric acids, and being precipitated unchanged on dilution; apparently it is not acted on by fused potash. On heating it with absolute alcohol and potash, a deep crimson solution is formed, which deposits bronze-coloured crystals on cooling; on exposure to moist air, or on mixing with water, the crimson solution turns green and yellow, and the quinone is reprecipitated. The quinone is reduced if heated with zinc and acetic or chlorhydric acid in a sealed tube at 150° C. The product is a resin, soluble in alcohol and ether, the dilute ethereal solution showing a splendid blue fluorescence. A similar resinous product is formed by the action of iodine, phosphorus and water, but in this case the principal products are volatile. These resinous products contain from 4·7 to 5 per cent. of oxygen, showing that 40 per cent. of the quinone is unreduced, and in fact it gradually separates from the resin in rhombic crystals. Analysis shows the composition of the reduction product to be $C_{18}H_{22}$ (m. p. 72° ?).

If the quinone be heated with soda-lime and zinc, it yields a hydrocarbon melting at 194°, which crystallises from alcohol in four-rayed stars composed of twinned rhombic plates.

Dibromotectoquinone is obtained by the action of bromine at 100—140°. It crystallises in orange-yellow, slender needles, which are generally arranged in spherical clusters, soluble in ether and alcohol. On fusion it melts at 165°; with potash it gives a blue or purple melt: this dissolves in water, forming a purple solution, from which acids throw down a yellow flocculent precipitate, no doubt a dihydroxyquinone.

Dinitrotectoquinone is a yellow powder obtained by the action of nitrosulphuric acid on the quinone. It is converted by sodium-amalgam, or zinc and caustic soda, into a crimson substance.

If the quinone be heated for two hours with nitrosulphuric acid, and the solution be then diluted, a purple precipitate is produced, which dissolves in alkalis, forming a purple solution.

Tectoquinone may possibly be retenequinone, which has not yet been discovered. Retene melts at 99° C.; the product of the reduction of tectoquinone softens at 70—72°, but it is evidently a mixture.

95. "The decomposition of Nitroethane by Alkalis." By Wyndham R. Dunstan and T. S. Dymond.

The authors have been engaged during the present year in studying the action of alkalis and of certain reducing agents on nitroethane. They observed in October, 1887, that nitroethane is gradually decomposed at ordinary temperature by contact with potassium carbonate

or its aqueous solution; at 80—90° the action is completed in a few hours. The chief products of the change are potassium nitrite and an oily liquid having the formula C_6H_9NO, which boils at about 170°, decomposing at a somewhat higher temperature, with the formation of what appears to be a pyridine derivative. The compound is not attacked when heated for 48 hours in a closed tube with concentrated chlorhydric acid, neither is it appreciably affected by reducing agents. It is readily oxidised by permanganate. It does not seem to be either a nitroso- or isonitroso-derivative. This compound is apparently identical with that described by Götting (*Annalen*, **243**, 104), who obtained it in Geuther's laboratory by heating together propyl iodide, sodium nitroethane and sodium ethoxide. Its ready formation, together with potassium nitrate, from nitroethane by contact with potassium carbonate, is likely to have an important bearing on the question as to the constitution of the paraffinoid nitro-compounds, and the authors therefore intend to continue the investigation. They are induced to publish the present preliminary notice by the appearance, in a recent number of the *Berichte* (November, 1888, p. 710), of an abstract of a paper by Sokolow in the *Russian Chemical Journal*. It is there shown that by heating nitroethane to 100—130° in closed tubes with sodium hydroxide or carbonate, the compound C_6H_9NO, described by Götting, is produced, and that if an alkyl iodide is present it takes no part in the change. Neither sodium hydroxide nor sodium carbonate attacks nitroethane at ordinary temperatures.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

A Correlation Theory of Chemical Action and Affinity, by T. W. Hall. London. 1888.

From the Publishers, Messrs. Remington and Co.

A Text-Book of Practical Organic Chemistry, by Chapman Jones, Third edition. London. 1888.

From the Publisher, Mr. J. Hughes.

Report (Chemical and Bacteriological) on the Atmosphere of Twenty-six Buildings in Newcastle-on-Tyne, by P. P. Bedson, T. W. Lovibond, and W. D. Severn. Newcastle-on-Tyne. 1888. (Pamphlet.)

From the Authors.

Pharmaceutical Journal. Series I. Vols. 1—13. Series II. Vols. 7—11. (For the Circulating Library.)

From W. F. Lowe, Esq.

II. *By Purchase.*

Grundriss der Elektrometallurgie, bearbeitet von C. A. M. Balling. Stuttgardt. 1888.

Ammoniak and Ammoniak-Preparate, von R. Arnold. Berlin, 1889.

Einleitung in die chemische Krystallographie, von A. Fock. Leipzig. 1888.

Grundlinien zu einer Physiologie des Gerbstoffes, von G. Kraus. Leipzig. 1888.

Chemie der organischen Farbstoffe, von R. Nietzki. Berlin. 1888.

Grundriss der Arzneimittellehre, von O. Schmiedeberg. Zweite Auflage. Leipzig. 1888.

Praktische Uebungen in der Maasanalyse, von C. Winkler. Freiberg. 1888.

Tabellen zur quantitativen Bestimmung der Zuckerarten, von E. E. Wein. Stuttgart. 1888.

Chemische Abhandlungen, 1838—1888, von C. F. Rammelsberg. Berlin. 1888.

Die Theerfarben mit besonderer Rücksicht auf Schädlichkeit und Gesetzgebung, hygienisch- und forensisch-chemisch untersucht, von T. Weyl. Erste Lieferung. Berlin. 1888.

Ueber Branntwein, seine Darstellung und Beschaffenheit in Hinblick auf seinen Gehalt an Verunreinigungen, von E. Sell. Berlin. 1888.

Renati Descartes Principia Philosophiae. 4to. Amstelodami 1664.

Remarks on the New Philosophy of Descartes, by E. Howard. 4to. London 1701.

History of Philosophy, by T. Stanley. Third edition. Folio. 1750.

M. Martini Lipenii Bibliotheca Realis Philosophica. Folio. Francofurti ad Moenum 1682.

Hermetis Aegyptorum et Chemicorum Sapientia ab Hermanni. Conringii animadversionibus vindicata per Olaum Borrichium, 4th Hafniae 1674.

Joh. Joachimi Beccheri Physica Subterranea. 4to. Lipsiae 1738.

A Collection of Lectures—Physical, Mechanical, Geographical, and Astronomical, by R. Hooke. 4to. London 1679.

Conspectus Chimiae, auctore D. Joanne Junckero 1744.

Mémoire sur la liquéfaction de l'oxygène et de l'hydrogène, par R. Pictet. Genève 1878.

L'alchimie et les alchimistes, par L. Figuier. Paris 1860.

La chimie enseignée par la biographie de ses fondateurs, par F. Hoefer. Paris 1865.

Chemistry, by A. Crum Brown. London 1875.

Praktische Spectralanalyse irdischer Stoffe, von H. W. Vogel. Zweite Auflage. Erster Theil, Qualitative Spectralanalyse. Berlin 1888.

Geschichte der Chemie von den ältesten Zeitenbiszur Gegenwart, zugleich Einfuhrung in das Studium der Chemie, von E. v. Meyer. Leipzig 1888.

Vierzehnter bis Siebzehnter Jahresbericht der k. chemischen Centralstelle für öffentliche Gesundheitspflege in Dresden. Herausgegeben von H. Fleck. Dresden 1888.

Arbeiten des pharmakologischen Institutes zu Dorpat. Herausgegeben von R. Kobert. Heft II. Stuttgart 1888.

HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY, ST. MARTIN'S LANE.

ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 60. Session 1888–89.

December 20th, 1888. Mr. W. Crookes, F.R.S., President, in the Chair.

Mr. Frank Bower was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. P. Carmody, F.I.C., The Laboratory, Somerset House; Edward Mitchell Chaplin, Westgate, Wakefield; John Curragh, Donaghadee, Belfast; David Ferrier, The Cottage, 50, High Street, Montrose; Conrad Gerland, Church, Lancashire; Alfred Miall Hanson, The Marjorie, Whalley, near Blackburn; Henry Joshua Phillips, Great Western Railway Laboratory, Swindon; Thomas John Underhill, 43, Chapel Road, West Norwood, S.E.

The following papers were read :—

96. "On some Leadhills Minerals." By Norman Collie, Ph.D.

Up to the present time, the analyses of the rare lead minerals which are to be found at the Leadhills in the southern highlands of Scotland, have been both meagre and contradictory. The author communicates a number of analyses of some specimens of leadhillite, lanarkite, vanadinite and other minerals, obtained from Dr. Wilson of Wanlockhead, Leadhills, and also of a considerable number collected by himself. The investigation was undertaken for two reasons; the chief one being to ascertain whether in the large number of double carbonates, sulphates, phosphates, &c., found at Leadhills, the constituent salts were always present in molecular proportions, or whether they were only isomorphous mixtures. The other reason was to determine which among the conflicting analyses met with in the mineralogical treatises were the most probably correct. Two new minerals were met with :—(1.) A pyromorphite, containing both copper oxide and vanadic acid; (2.) an aragonite in which part of the calcium carbonate had been displaced by lead carbonate.

The other minerals analysed were leadhillite, lanarkite, caledonite, linarite, vanadinite, pyromorphite, plumbocalcite, calamine, dolomite, and strontianite.

97. "Metallic Derivatives of Halogen Nitrophenols." By Arthur R. Ling.

Chlorobromoparanitrophenol, prepared by brominating chloroparanitrophenol, m. p. 110°, in acetic acid solution, separates from boiling water in colourless crystals melting at 137° with decomposition. The following metallic derivatives of this phenol are described:—

Potassium salt, $C_6H_2ClBrNO_3K\cdot H_2O$, golden-yellow needles.
Calcium salt, $(C_6H_2ClBrNO_3)_2Ca\cdot 9H_2O$, yellow needles.
,, $(C_6H_2ClBrNO_3)_2Ca\cdot 4H_2O$, yellow plates.
Barium salt, $(C_6H_2ClBrNO_3)_2Ba\cdot 10H_2O$, yellow needles.
,, $(C_6H_2ClBrNO_3)_2Ba\cdot 3\frac{1}{2}H_2O$, red needles.

The calcium-derivatives of the following were also examined:—

Dibromorthonitrophenol, red plates, containing 7 mols. H_2O.
Dichlororthonitrophenol, orange-yellow fibrous needles containing 1 mol. H_2O.
Dichlororthonitrophenol, red crystals, containing 4 mols. H_2O.
Parachlororthobromorthonitrophenol, red plates, containing $4H_2O$.
Parabromorthoiodorthonitrophenol, red plates, containing $4H_2O$.

They are almost insoluble in cold and only sparingly soluble in boiling water.

A general feature of the calcium-derivatives of the nitrophenols, especially those of the orthonitro-series, seems to be the difficulty with which the water of crystallisation is removable on heating, *e.g.*, it was found impossible to completely dehydrate calcium dibromorthonitrophenol below a temperature at which it decomposed. The author also points out that as they lose their water of crystallisation, the calcium orthonitrophenol-derivatives change from red to an orange colour, which is at variance with the conclusions of Carnelley and Alexander.

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ABSTRACTS OF THE PROCEEDINGS

OF

THE CHEMICAL SOCIETY.

Vol. V. Nos. 61—75.

JANUARY—DECEMBER, 1889.

EDITED BY THE SECRETARIES.

LONDON:
GURNEY & JACKSON, 1, PATERNOSTER ROW.
1889.

LONDON:
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DATES OF ISSUE OF THE MONTHLY NUMBERS OF THE JOURNAL OF THE CHEMICAL SOCIETY TO FELLOWS.

January number	was issued	10th January.
February	„	5th February.
March	„	8th March.
April	„	6th April.
May	„	21st May.
June	„	4th June.
July	„	10th July.
August	„	3rd August.
September	„	1st September.
October	„	9th October.
November	„	2nd November.
December	„	11th December.
Index	„	will be issued early in January.

LIST OF GRANTS MADE FROM THE RESEARCH FUND DURING THE YEAR.

£50 to Professor Meldola for the investigation of the isomerism of mixed diazo-compounds.

£50 to Professor W. H. Perkin, jun., for the continuation of his researches on the synthetical formation of closed carbon chains.

LIST OF FELLOWS ELECTED DURING 1889.

Name.	Proposed.	Elected.
Abrahall, Hoskyns J. L.	February 21st	April 4th.
Addyman, Frank S.	June 4th	December 5th.
Annal, James	February 21st	April 4th.
Bailey, Richard D.	February 21st	April 4th.
Baker, Charles F.	June 4th	December 5th.
Barnes, Charles L.	December 6th, 1888	January 17th.
Barry, Collis T. D.	February 7th	April 4th.
Bell, Edward W.	May 2nd	June 20th.
Bell, Percy Carter	November 1st, 1888	January 17th.
Boam, Frederick W.	March 7th	April 4th.
Butcher, William F.	November 7th	December 5th.
Burgess, John	November 7th	„ „
Broadbent, Harry	February 7th	April 4th.
Cargill, William D.	May 16th	June 20th.
Carnody, P.	December 20th, 1888.	February 21st.
Chaplin, Edward M.	„ „	„ „
Clayton, John W.	January 17th	„ „
Cook, Edward B.	February 7th	April 4th.
Cooper, Albert	December 6th, 1888	January 17th.
Coste, Frank H. P.	November 7th	December 5th.
Cridland, Francis E. J.	February 7th	April 4th.
Cunningham, Alexander A.	„ „	„ „
Curragh, John	December 20th, 1888.	February 21st.
Dixon, William H.	December 6th, 1888	January 17th.
Dott, David B.	November 7th	December 5th.
Duisberg, Carl	November 15th, 1888.	January 17th.
Dukes, Thomas W.	June 20th	December 5th.
Easterfield, Thomas H.	February 7th	April 4th.
Edwards, Robert S.	November 7th	December 5th.
Erskine, James K.	„ „	„ „
Evans, Philip N.	January 17th	February 21st.
Ferguson, Robert	January 17th	February 21st.
Ferrier, David	December 20th, 1888.	„ „
Foggie, John	November 7th	December 5th
Ford, John S.	June 4th	„ „
Freestone, Joseph T.	February 7th	April 4th.
Frew, William	March 7th	„ „
Garrett, Frederick C.	December 6th, 1888	January 17th.
Gibbs, William T.	April 18th	May 16th.
Gerland, Conrad	December 20th, 1888.	February 21st.
Goldsmith, Byron B.	April 18th	May 16th.
Gott, B. S.	December 6th, 1888	January 17th.
Gow, Robert J.	„ „	„ „
Grist, Charles J.	April 18th	May 16th.
Gripper, Harold	November 7th	December 5th.
Gudeman, Edward	December 6th, 1888	January 17th.

Name.	Proposed.	Elected.
Hall, Allan T.	December 6th, 1888.	January 17th.
Hall, James	March 7th.	April 4th.
Hall, John A.	December 6th, 1888.	January 17th.
Hanson, Alfred M.	December 20th, 1888.	February 21st.
Helbing, H. B.	November 7th	December 5th.
Hickey, John J.	January 17th	February 21st.
Hoyle, Richard A.	February 7th	April 4th.
Hoyles, Henry R.	February 21st	„ „
Howard, John W.	May 2nd	June 20th.
Hughes, Robert E.	November 7th.	December 5th.
Ingle, Herbert	February 7th.	April 4th.
Jackson, Eric H.	June 20th	December 5th.
Jowett, William H.	January 17th	February 21st.
Kay, James R.	November 7th.	December 5th.
Kerwood, Henry R.	„ „	„ „
Kitchin, John	March 21st	May 16th.
Knight Frederick C.	May 2nd	June 20th.
Knott, Frederick T.	November 7th	December 5th.
Lauer, William E.	January 17th	February 21st.
Leaper, Clement J.	February 21st	April 4th.
Ledingham, L. Napier	November 7th	December 5th.
Legg, John E.	March 21st	May 16th.
Leigh, Cecil	December 6th, 1888.	January 17th.
Lennox, Lionel R.	November 15th, 1888	„ „
Lloyd, George	„ „	„ „
Maeleroy, Arthur L.	December 6th, 1888.	January 17th.
McAlman, George.	January 17th	February 21st.
McMurtry, George C.	March 7th.	April 4th.
McNally, Christopher J.	February 7th	„ „
Mason, G. B.	November 7th	December 5th.
Mason, James B.	„ „	„ „
Mercer, Thomas	„ „	„ „
Miller, James B.	March 7th.	April 4th.
Miller, Harry E.	January 17th	February 21st.
Morgan, Arthur F.	„ „	„ „
Morrow, Henry W.	May 16th	June 20th.
Muir, James	November 15th, 1888.	January 17th.
Nesbitt, William B.	February 7th	April 4th.
Nettleton, Joseph A.	November 7th.	December 5th.
Newsholme, George T.	February 21st.	April 4th.
Nickels, Wallace C.	November 7th.	December 7th.
Norman, J. T.	June 4th	December 5th.
O'Mahoney, D.	May 2nd	June 20th.
Parker, James G.	November 7th.	December 5th.
Parker, Robert H.	November 15th, 1888	January 17th.
Peace, Frank K.	December 6th, 1888.	„ „
Percival, John	November 15th.	„ „
Phillips, Benjamin	May 2nd	June 20th.
Phillips, Henry J.	December 20th, 1888	February 21st.

Name.	Proposed.	Elected.
Pike, Alfred E.	November 7th	December 5th.
Ping, William	„ „	„ „
Pingstone, George A.	January 17th	„ „
Platt, John C.	March 7th.	April 4th.
Priestley, Charles W.	December 6th, 1888.	January 17th.
Proctor, Charles	February 7th	April 4th.
Provis, John	December 6th, 1888	January 17th.
Quincke, Frederick	November 7th	December 5th.
Ransom, Francis	April 4th	May 16th.
Read, Arthur A.	February 7th	April 4th.
Reckitt, Ernest	„ „	„ „
Redwood, Robert	May 16th	June 20th.
Richards, Duncan T.	March 7th.	April 4th.
Richards, Edgar	December 6th, 1888	January 17th.
Richards, Percy A. E.	November 15th, 1888	„ „
Roberts, Emanuel	May 2nd	June 20th.
Roberts, Richard W.	February 21st.	April 4th.
Robins, Harry H.	January 17th	February 21st.
Ruhemann, Siegfried	December 6th, 1888	January 17th.
Shegog, Thomas A.	February 21st.	April 4th.
Sibson, Alfred E	April 18th	May 16th.
Simmonds, Henry	February 21st.	April 4th.
Singer, Ignatius	April 18th	May 16th.
Slater, John W.	March 7th.	April 4th.
Southam, Stanley	January 17th	February 21st.
Speakman, James	„ „	„ „
Steel, Sydney	June 4th	December 5th.
Stillman, Thomas B.	January 17th	February 21st.
Swan, Robert M. W.	May 2nd	June 20th.
Sworn, Sydney A.	November 7th	December 5th.
Sykes, Walter J.	March 21st	May 16th.
Tingle, John B.	June 4th	December 5th.
Tucker, Willis G.	November 7th	„ „
Turpin, George L.	January 17th	February 21st.
Underhill, Thomas J.	December 20th, 1888.	February 21st.
Venis, Walter	December 6th, 1888.	January 17th.
Vine, Henry C. A.	February 7th	April 4th.
Virtue, William	March 21st.	May 16th.
Voss, Walter A.	February 7th	April 4th.
Walker, Daniel	November 7th	December 5th.
Waterhouse, William J.	March 7th.	April 4th.
Weir, Patrick A.	February 21st	„ „
White, John J.	February 7th	„ „
Whitehouse, William	June 20th.	December 5th.
Whittam, Matthew	November 7th	„ „
Wigan, Basil P.	„ „	„ „
Wilkie, John	„ „	„ „
Wiltshire, John	„ „	„ „
Wood, Charles	February 21st	April 4th.
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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 61. Session 1888–89.

January 17th, 1889. Mr. W. Crookes, F.R.S., President, in the Chair.

Messrs. Arthur G. Bloxam, T. O. Sandell and Walter Tate were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. John William Clayton, Blackburn; Philip Norman Evans, Nash Mills, Hemel Hempstead; Robert Ferguson, M.A., Burgh School, Linlithgow, N.B.; John Joseph Hickey, Beech Mount, Harpurley; William Hall Jowett, Blackburn; William Eggleston Lauer, Chemisches Laboratorium, Georgen Strasse 35, Berlin; George McAlman, 246, Bath Street, Glasgow; Harry East Miller, 1264, 14th Street, Oakland, California, U.S.; Arthur Frederick Morgan, 21, Rumford Street, Manchester; George Arthur Pingstone, Yew Bank, Brook Road, Heaton Chapel; Harry Holliss Robins, 11, Mecklenburgh Street, W.C.; James Speakman, 4, Craigisbank Terrace, Dundee; Stanley Southam, 7, Ritson Road, Dalston, N.; Thomas B. Stilleman, 358, Bloomfield Street, Hoboken, New Jersey, U.S.A.

The following were duly elected Fellows of the Society:—Messrs. Charles Lightfoot Barnes, Percy Carter Bell, Albert Cooper, William Hepworth Dixon, Dr. Carl Duisberg, Frederick Charles Garrett, B.Sc., B. S. Gott, B.A., Robert J. Gow, Edward Gudeman, Ph.B., Allan Twistleton Hall, John A. Hall, Cecil Leigh, Lionel Remond Lenox, Ph.B., George Lloyd, Arthur Lloyd Mackeroy, M.A., James Muir, Robert Hodgson Parker, Charles W. Priestley, B.Sc., Frank R. Peace, John Percival, B.A., John Provis, Edgar Richards, Percy Andrew Ellis Richards, Siegfried Ruhemann, Ph.D., M.A., Walter Venis.

The following papers were read:—

1. "A cubical form of Bismuthous Oxide." By M. M. Pattison Muir and Arthur Hutchinson.

A puce-coloured precipitate is produced by adding excess of potassium cyanide to a boiling solution of bismuth nitrate in dilute nitric acid. Boedeker (*Annalen*, **123**, 61) gave the formula $Bi_2O_5 \cdot 2H_2O$ to this substance; according to C. Hoffmann (*Annalen*, **223**, 110), however, the precipitate is Bi_2S_3, the sulphur being derived from impurity in the cyanide; and one of the authors has described it as an oxycyanide of bismuth (*Proc. Roy. Soc. Edin.*, **11**, 557). Further experiments show that the precipitate is a compound of Bi, C, N, and O. When this precipitate, without being washed, is repeatedly treated with boiling concentrated potash solution, 2—3 per cent. of the bismuth in the precipitate goes into solution with practically the whole of the carbon and nitrogen, and tetrahedral crystals of bismuthous oxide remain. It is almost impossible to free these crystals from an adhering film of the puce-coloured compound by treatment with potash; very long-continued action of boiling potash—so concentrated that it solidifies on cooling—does, it is true, remove the last trace of the carbon and nitrogen compound, but the crystals are much corroded by this action. To obtain the cubical form of bismuthous oxide free from the puce-coloured compound, it is better to remove the last traces of this substance by heating for a short time to full redness in air. Cubical bismuthous oxide has the density 8·838 at 25° relatively to water at the same temperature; the relative density of the ordinary rhombic bismuthous oxide is 8·3.

2. "Cupric Iodide and the interaction of Iodides with Cupric salts." By D. J. Carnegie, B.A.

By digesting cuprous iodide with iodine and water in a tightly closed bottle at 80° for a few minutes, the author has obtained solutions of cupric iodide containing as much as 0·82 gram per 100 c.c., but has been unable to obtain cupric iodide in the solid state, either from such solutions or by other means. A well-defined basic periodide, $[CuI_2 2CuO \cdot 4H_2O]$, was obtained by digesting copper with barium iodide. The author attempts an explanation of the fact that concentrated solutions of cupric iodide are not obtainable from the interaction of soluble iodides and cupric salts, or of iodhydric acid and cupric hydroxide, in terms of (1) the affinity which iodhydric acid and iodides generally possess for iodine; and (2) the disturbance of equilibrium which the separation of solid iodine causes in a medium which holds cupric iodide in solution. He regards the usual reason given for the non-existence of cupric iodide, viz., its intrinsic instability, as probably inadequate.

3. "Periodates." Part II. By C. W. Kimmins.

The following salts are described :—

Lead Salts.—The interaction of lead nitrate and $K_4I_2O_9$ or $Na_2H_3IO_6$ results in the production of $Pb_3H_2(IO_6)_2$. When the salt was dissolved in nitric acid, and the solution was concentrated, $Pb_3(IO_5)_2$ was formed. By boiling the first salt with concentrated nitric acid, $Pb(IO_4)_2$ was produced. The salt $Pb_3(IO_5)_2$ is formed by heating $Pb_3H_4(IO_6)_2$ to 275° for four hours. These lead periodates are more or less insoluble in nitric acid; the more insoluble salts are lighter in colour than the others; the more soluble salts show a tendency to take up moisture.

Iron Salts.—On treating $Na_2H_3IO_6$ or $K_4I_2O_9$ with ferric chloride, a light-brown precipitate was obtained, which on drying at 100° formed a red powder, $FeHI_2O_9$; when this was boiled with nitric acid, the salt $Fe(IO_4)_3$ was produced. The ferrous salt, $Fe_5(IO_6)_2$, was obtained from $Na_2H_3IO_6$, and the salt, FeH_3IO_6, from $K_4I_2O_9$.

Copper Salts.—The green salt, Cu_2HIO_6, was obtained both from $Na_2H_3IO_6$ and $K_4I_2O_9$. On dissolving this salt in nitric acid and concentrating, a yellow salt was produced, probably $Cu(IO_4)_2$.

Nickel Salts.—No salt corresponding to HIO_4 could be obtained. The salt $Ni_3(IO_5)_2$ is greenish-yellow, and $Ni_2I_2O_9$ is black and crystalline.

Cadmium Salts.—The only salt obtained was $CdHIO_5$; it is easily prepared from $Na_2H_3IO_6$, and with difficulty from $K_4I_2O_9$.

Silver Salts.—The salt $Ag_4I_2O_9$ was formed by treating $K_4I_2O_9$ with silver nitrate; by treating this with nitric acid of different degrees of concentration, other silver periodates are formed. All silver salts yielded orange crystals of $AgIO_4{\cdot}H_2O$ when heated with concentrated nitric acid.

The salts described in this and a previous paper may be thus classified :—

Meta-periodates. Salts of HIO_4.	Meso-periodates. Salts of H_3IO_5.	Para-periodates. Salts of H_5IO_6.	Di-periodates. Salts of $H_4I_2O_9$.
$AgIO_4{\cdot}H_2O$	Ag_2HIO_5	$Na_2H_3IO_6$	$K_4I_2O_9$
$AgIO_4$	$Pb_3(IO_5)_2$	$Na_3H_2IO_6$	$K_3HI_2O_9$
$Pb(IO_4)_2$	$Ni_3(IO_5)_2$	$Ba_5(IO_6)_2$	$Ag_4I_2O_9{\cdot}3H_2O$
$Fe(IO_4)_3$	$CdHIO_5$	$Ag_2H_3IO_6$	$Ag_4I_2O_9{\cdot}H_2O$
$Cu(IO_4)_2$		$Ag_3H_2IO_6$	$Ag_4I_2O_9$
		$Pb_3H_4(IO_6)_2$	$FeHI_2O_9$
		$Fe_5(IO_6)_2$	$Ni_2I_2O_9$
		FeH_3IO_6	
		Cu_2HIO_6	

4. "Compounds of Arsenious Oxide with Sulphuric Anhydride." By R. H. Adie.

This paper describes in detail the preparation of a series of compounds of As_2O_3 and SO_3; the compounds are represented by the formula $As_2O_3 \cdot xSO_3$, where $x = 1, 2, 4$, and 8. $As_2O_3 \cdot 8SO_3$ is produced by the interaction of arsenious oxide and sulphuric anhydride; when fuming sulphuric acid is used, approximately $2H_2SO_4 \cdot SO_3$, $As_2O_3 \cdot 4SO_3$, and probably also $As_2O_3 \cdot SO_3$ are formed; $As_2O_3 \cdot 2SO_3$ is obtained by using ordinary concentrated sulphuric acid; and when acids are used approximately corresponding to the formulæ of $9H_2SO_4 \cdot 2H_2O$, $9H_2SO_4 \cdot 4H_2O$, $9H_2SO_4 \cdot 6H_2O$, and $H_2SO_4 \cdot H_2O$, the product has the composition $As_2O_3 \cdot SO_3$. Sulphuric acid of greater dilution than $H_2SO_4 \cdot H_2O$ was found not to yield any compound of As_2O_3 with SO_3. All the compounds described are easily decomposed by moisture, or by heating.

5. "On a compound of Boric Acid with Sulphuric Anhydride." By R. F. D'Arcy, B.A.

On adding an excess of sulphur trioxide to boric acid, and heating the mixture until sulphur trioxide ceases to be evolved, a substance remains which is fairly stable and possesses the composition $BH_3O_3 \cdot 3SO_3$. This formula may be written $B(HSO_4)_3$, but sufficient experiments have not yet been made to determine whether the compound is a sulphate of boron or a compound of boric acid with sulphuric anhydride. In analysing the compound, use was made of Gooch's accurate method of estimating boric acid by distillation with methyl alcohol (*Proc. Am. Acad. of Arts and Sciences*, 1886—1887). Merz and Schultz-Sellack have described compounds of the formulæ $5B_2O_3 \cdot 2SO_3 \cdot 2H_2O$ and $B_2O_3 \cdot 3SO_3 \cdot H_2O$. Attempts to obtain results similar to those obtained by these chemists were unsuccessful. The percentage composition given by the formula of Schultz-Sellack, and that given by the formula $H_3BO_3 \cdot 3SO_3$, together with the experimental numbers obtained, are stated in the following table:—

	Schultz-Sellack. $B_2O_3 \cdot H_2O \cdot 3SO_3$.	$H_3BO_3 \cdot 3SO_3$.	Results of analyses.			
			(1.)	(2.)	(3.)	(4.)
SO_3 ..	73·2	79·5	78·8	79·7	78·3	80·1
B_2O_3 .	21·2	11·6	11·3	10·6	12·2	11·8
H_2O..	5·5	8·9	9·9 (by diff.)	9·7 (by diff.)	8·9 (by diff.)	8·1 (by diff.)

6. "Notes of experiments on Butter Fat." By A. Wynter Blyth and G. H. Robertson.

The authors have endeavoured to separate the glycerides of butter fat by (*a*) fractional crystallisation of the solid portion from alcohol; (*b*) dissolution in ether and fractional precipitation by alcohol; (*c*) electrolysis. The main result of their experiments is to show that butter fat is composed of solid crystalline fats and an oil. The proportion of the oil to the solid crystalline fats is about 45·5 of butter oil to 54·5 butter crystals. A crystalline glyceride was separated, to which the authors ascribe the formula $C_3H_5\begin{cases}C_4H_7O_2.\\C_{16}H_{31}O_2.\\C_{18}H_{34}O_2.\end{cases}$

They consider that butter is mainly made up of compound and not of simple triglycerides.

To the original paper is added a note of the electrical resistance of butter fat and olive oil.

7. "Gawalowski's method for the volumetric estimation of Sulphuric Acid." By Barker North, Assoc. N.S.S.

In Fresenius' *Zeitschrift für analytische Chemie* for 1888, **27**, 152—159, is a paper on the "Volumetric estimation of combined Sulphuric Acid," by A. Gawalowski. As such a method is still a desideratum among chemists, I undertook, at the request of Professor Thorpe, to make a critical examination of Gawalowski's process. The method consists in adding a quantity of a standard solution of barium chloride, more than sufficient to precipitate the sulphuric acid which may be present, and titrating the excess of barium chloride with a standard solution of sodium carbonate, using phenolphthaleïn as an indicator of the excess of sodium carbonate.

The barium chloride solution was made as nearly seminormal as possible by weighing, and then accurately standardised by gravimetric analysis. The sodium carbonate solution was made seminormal by weighing out recently ignited Na_2CO_3. A series of experiments were made with strict adherence to Gawalowski's instructions. The errors ranged from 2 to 27·5 per cent. It will thus be seen that the method is entirely worthless. The cause of the error doubtless is the solubility of the barium carbonate, which, even in the presence of alcohol, affects the phenolphthaleïn to such an extent as to render it impossible to properly detect the true end point of the interaction.

8. "Note on the 1 : 3 homo- and the isomeric hetero-$a\beta$-dichloronaphthalenes melting at nearly the same temperature." By Henry E. Armstrong and W. P. Wynne.

In a recent communication (*Chem. Soc. Proc.*, 1888, 104) we have

specially called attention to the fact first brought under notice by one of us at the Manchester meeting of the British Association, on September 2nd, 1887 (*B. A. Report*, 1887, 231), that *two* $\alpha\beta$-dichloronaphthalenes exist which melt nearly at the same temperature, slightly above 60°. Cleve, in a paper in the number of the *Berichte* issued previously in the same week as the number of the Proceedings containing our note, without any reference to our earlier work, corroborates our conclusion (p. 3275), but continues to assign the same melting point (61°) to the two isomers. Cleve's earlier statement (*Ber.*, 1886, 2182) that two of the isomeric nitrosulphonic acids obtained on nitrating naphthalene-β-sulphonic acid both gave the dichloronaphthalene melting at 61° evidenced his belief, and led others to the belief, that isomeric change took place during the treatment of the sulphochlorides with PCl_5; he subsequently pointed out, however, that perhaps there were two isomeric dichloronaphthalenes melting at 61°. Our observation published in 1887 first proved that no isomeric change takes place, and thus deprived the objections which had been urged against the use of PCl_5 in determining the constitution of nitro- and sulphonic derivatives of naphthalene of their force. Erdmann, in the number of the *Berichte* just issued (1888, 3446), states that Reverdin and Nölting were the first to positively state that two dichloronaphthalenes melting at 61° exist; it is to be noted, however, that Professor Nölting was present at the meeting at which one of us brought forward the above-mentioned facts, and that Reverdin and Nölting's invaluable monograph was at that time only in the press.

In the notice referred to, Erdmann speaks of Cleve's recognition of two dichloronaphthalenes melting at 61° as an important confirmation of *his* views (*Annalen*, **247**, 308) as to the stability of isomeric naphthalene-derivatives; and he states that, disregarding the changes which occur in the case of sulphonic acids when heated with water or sulphuric acid—which he has made the subject of special experimental investigation—no case is now known of the conversion of a naphthalene-derivative into a "position-isomer." These statements afford multiple illustration of simple belief in the sufficiency of the *Berichte* and a very few other German journals as media of communication among chemists which is becoming so noticeable. The manner in which isomeric change takes place in the case of naphthalene-derivatives has been specially discussed and referred to by one of us (*Chem. Soc. Trans.*, 1887, 266, 587; *B. A. Report*, 1886, 216; 1887, 231; 1888; *Chem. News*, **58**, 295; *Chem. Soc. Proc.*, 1887, 143—146). A number of cases of isomeric change have been described by us, one so far back as 1881, and that, too, in the *Berichte* (1882, 204), although perhaps this case may be denied rank as one of change

into a "position-isomer" by Erdmann; and we shall shortly have to describe other cases.

In the same paper Erdmann makes an acceptable addition to our knowledge in describing the synthesis of the 1 : 3-dichloronaphthalene melting at 61·5° from 1 : 3-dichlorobenzaldehyde. He, however, forgets to mention that the constitution of this dichloronaphthalene had already been determined by us; he calls attention to the existence of two dichloronaphthalenes melting at almost the same temperature as though it were an original observation; and he states that it will be his "nächste Aufgabe" to sufficiently determine the chemical differences of the two isomers in question and to discover means of discriminating between them with certainty: overlooking the fact that we have long since stated that we are engaged in further characterising the isomeric dichloronaphthalenes; and that in our recent note, to the admirable and almost verbal translation of which in that most valuable periodical the *Chemiker Zeitung* he refers and therefore has under notice, we have already described certain distinctive properties and have made the identification of the two dichloronaphthalenes in question a simple matter.

The description originally given by Erdmann and Kirchhoff of the dichloronaphthalene melting at 61·5° which they obtained from parachlorobenzaldehyde did not suffice to determine its identity, and as it was all-important to us to place the constitution of the two dichloronaphthalenes now under discussion beyond question, we have been at the pains to prepare it by Erdmann and Kirchhoff's method from parachlorotoluene. In doing this we have had cause to appreciate and value their labours. By heating the chloronaphthol with PCl_5, a product was obtained consisting of a mixture of tri- and di-chloronaphthalene; these were approximately separated by crystallising from alcohol the tri-derivative separating first in prisms melting at 120°. The residual dichloronaphthalene fused at 57—59°, and as the quantity was inconsiderable this was converted directly into sulphonic acid, from which salts and the chloride were prepared. The potassium salt was found to be sparingly soluble in water containing a little potassium carbonate, and crystallised in anhydrous scales; the sulphochloride crystallised from benzene in needles, becoming opaque on standing and melting at 117°. The dichloronaphthalene recovered from the sulphochloride by hydrolysis *melted at* 63·5°. There can be no doubt therefore that the dichloronaphthalene prepared synthetically by Erdmann and Kirchhoff's method is identical with that from Arnell's betachloronaphthalenesulphonic acid and from the betanaphthylaminesulphonic acid known as the Badische modification. Our previous conclusion that these acids are heteronucleal derivatives is thus confirmed.

Erdmann has entirely misunderstood our objections to his conclusions with respect to the constitution of the dichloronaphthalene melting at 63·5,° viz., that his method does not enable us to discriminate the 1 : 2′ from the 1 : 3′ modification. It is not that we think it necessary that the chlorophenylisocrotonic acid should have been isolated; our objection arises from our conviction that, as we have already said, "the origin of the hydroxyl in their acids cannot be determined." The oxygen-atom in the naphthol may be either that which originally was present in the carbonyl and which may have remained attached to the carbonyl-carbon atom; or it may be that which was contained in the carboxylic hydroxyl; or that which was contained in the aldehyde; and in the last two cases the OH-group may ultimately become associated with either of the two para-carbon atoms with which the oxygen-atom is represented as connected in the formula of phenylparaconic acid. There is at present, moreover, no valid reason to be urged against the conclusion that in some cases the OH-group may assume the one, in some other cases the other position, according to the nature of the influence exercised by the chlorine-atom. We are specially engaged with experiments in the hope of determining the exact constitution of the dichloronaphthalene melting at 63·5°.

9. "The constitution of betanaphthol-α-sulphonic acid (Bayer's acid)." By Henry E. Armstrong.

The number of the *Berichte* just issued contains a most valuable paper by Dr. O. N. Witt, on the reduction products of the azo-dyes derived from the various naphthol- and naphthyl-aminesulphonic acids, together with another discussing the constitution of betanaphthol-α-sulphonic acid—conventionally known as Bayer's acid. In the latter I regret to say that Dr. Witt altogether misrepresents my views, misreading an early paper of mine (*Berichte*, 1882, 200); and overlooking the discussion which took place after the reading of Mr. Green's paper on November 15th last, and the conclusions arrived at by Mr. Wynne and myself with regard to the amido-acid corresponding to Bayer's hydroxy-acid published in the same number of the Proceedings (p. 104).

Witt speaks of my having converted Bayer's acid into 1 : 2 bromobetanaphthol, and of my having in consequence inferred that Bayer's acid is the 1 : 2 modification; actually, however, in my paper, I describe (p. 202) the action of bromine on *betanaphthylsulphate*. I may quote the following passages from my Report to the British Association at the Manchester meeting in 1887, read, I believe, in Dr. Witt's presence, to show what have been my views:—

"The dichloronaphthalene obtained from Bayer's modification of β-naphtholsulphonic acid is doubtless hetero-θ-dichloronaphthalene; the conclusion arrived at by Claus that this acid is a 2 : 3 derivative is not only opposed to all that is known of the behaviour of naphthalene compounds, inasmuch as it involves the assumption that on sulphonating β-naphthol the second β-position contiguous to the hydroxyl becomes displaced; it is untrustworthy, as the dichloroquinone which he obtained may have been, and doubtless was, produced by the action of chlorine liberated during the process of oxidation.

"*Theory of the formation of azo-dyestuffs from β-naphthol.*—It is well known that in the case of β-naphthol itself the α-hydrogen atom contiguous to the OH-group becomes displaced by the azo-group. This position appears to be free in all the sulphonic acids which afford azo-colours, and those naphthol-derivatives in which it is not free appear to be incapable of forming such colours; it is therefore a legitimate inference that all azo-dyes derived from β-naphthol are formed by the introduction of an azo-group in the position indicated."

At the meeting on November 15th I "referred to Emmert's observation (*Annalen*, **241**, 371) that the betanaphtholsulphonic acid corresponding to betanaphthylamine-α-sulphonic acid is convertible into a dihydroxynaphthalene different from hydrobetanaphthaquinone as incompatible with the conclusion that the α-acid was the 1 : 2 compound;" and I again expressed the opinion "that an acid in which the SO_3H and OH groups were in the relative positions 1 : 2 would not be capable of forming azo-colours."

The conclusion which I had arrived at as to the probable constitution of the betanaphthol (and betanaphthylamine) azo-dyes, led me, in October, 1887, to commence their study precisely in the manner in which Witt has now done so skilfully and with such thoroughness; at my suggestion, Dr. F. Feist reduced the benzeneazobetanaphtholsulphonic acid prepared from Schaefer's acid, and found, as Witt has done, that the reduction product was identical with Meldola's amidobetanaphtholsulphonic acid; he obtained, by hydrolysing the acid, the known amidobetanaphthol, and converted it into betanaphthaquinone. Recently, having determined that Bayer's acid corresponded to the heteronucleal dichloronaphthalene melting at 63·5°, and that it is either a 1 : 2′ or 1 : 3′ derivative, I had commenced the study of the *Croceine* prepared from Bayer's acid and diazonaphthionic acid. Witt's results relieve me in a most welcome manner from pursuing the investigation. His discovery that the azo-group in the croceines is in the α-ortho-position is precisely what I had foreseen, and I have little doubt that when he examines the reduction products of the azo-dyes prepared from the other betanaphthol- and betanaphthylamine-

sulphonic acids, he will find that the azo-group is always introduced into the α-ortho-position contiguous to the OH-group of the naphthol, or the NH-group of the naphthylamine.

10. "The sulphonation of naphthalene-β-sulphonic acid." By Henry E. Armstrong.

The number of the *Berichte* just issued contains at p. 916 of the "Referate" an abstract of a patent secured by Ewer and Pick for a *new* naphthalenedisulphonic acid prepared by sulphonating naphthalene-β-sulphonic acid, or one of its salts, by means of fuming sulphuric acid. When this patent came under my notice some months ago, I at once came to the conclusion that the *new* acid was the (?) β-disulphonic acid prepared by Mr. Wynne and myself by a similar process by means of chlorosulphonic acid instead of fuming sulphuric acid, and described at the meeting of the Society on November 4th, 1886 (*Chem. Soc. Proc.*, 1886, 230). On preparing the acid according to Ewer and Pick's directions, this surmise proved correct. It may be added that this acid corresponds in constitution to η-dichloronaphthalene (m. p. 48°), and, therefore, to Dahl's modification of betanaphthylaminesulphonic acid. I am indebted to Mr. Garrett for assisting me to make the comparison.

At the next meeting, on February 7th, the following paper will be read:—

"Researches on the constitution of Azo- and Diazo-derivatives. Part V. Compounds of the Naphthalene-β-series" (*continued*). By R. Meldola, F.R.S., and G. T. Morgan.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 62. Session 1888–89.

February 7th, 1889. Mr. W. Crookes, F.R.S., President, in the Chair.

Messrs. Albert Cooper, W. Hepworth Dixon, F. C. Garrett, F. B. Guthrie, John Percival and R. W. Woosnam were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. T. D. Collis, Barry, Asirgarh, Central India; Harry Broadbent, 31, Victoria Terrace, Belle Vue Road, Leeds; Edward Barnwell Cook, Clifton College, Bristol; Francis Edward John Cridland, Mayfield, Southboro, Surbiton; Alexander Archie Cunningham, American Sugar Refinery, Battery Street, San Francisco, U.S.A.; Thomas Hill Easterfield, Clare College, Cambridge; Joseph T. Freestone, 33, Brownlow Road, New Ferry, Cheshire; Richard Ashworth Hoyle, 11, Market Square, Lytham; Herbert Ingle, Pool, near Leeds; Christopher J. McNally, M.D., Medical College, Madras; William Beattie Nesbitt, University of Toronto; Charles Proctor, 192, Barry Road, Dulwich, S.E.; Arthur Avery Read, Owens College, Manchester; Ernest Reckitt, Caen Wood Towers, Highgate, N.; Henry Charles Anslie Vine, 15, Old Pond Street, Bath; Walter Arthur Voss, Oak House, Croydon Road, Anerley; John Isawoo White, Rangoon College, Rangoon.

The following papers were read :—

11. "Researches on the constitution of Azo- and Diazo-derivatives. V. Compounds of the Naphthalene-β-series" (continued). By R. Meldola, F.R.S., and G. T. Morgan.

The authors describe the preparation of benzoyl-derivatives of azo-β-naphthol compounds by the displacement of the amido-group in the corresponding amido-derivatives by $C_7H_5O{\cdot}O-$ by means of the diazo-

interaction in the presence of benzoic acid. The method is analogous to that described last year by one of the authors and F. J. East (*Berichte*, 1888, 601; *Chem. Soc. Trans.*, 1888, 465) for the preparation of azophenylic acetates, action taking place in accordance with the equation $R{\cdot}N_2{\cdot}OH + HO{\cdot}C_7H_5O = R{\cdot}OC_7H_5O + N_2 + H_2O$.

The *metanitrobenzeneazobenzoate*, $(m)NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OC_7H_5O(3)$, has been prepared by the foregoing method, as well as by the direct benzoylation of metanitrobenzeneazo-β-naphthol by means of dry sodium benzoate and benzoyl chloride; it crystallises in orange needles melting at 171°. Benzeneazo-β-naphthol, when similarly treated with benzoyl chloride and sodium benzoate, gives *benzeneazo-β-naphthyl benzoate*, $C_6H_5{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OC_7H_5O$, which crystallises in dense, orange prisms melting at 125°. The greater portion of the paper is devoted to a study of the products of reduction of the azo-β-naphthol-derivatives containing acid radicles. When violently reduced with tin and chlorhydric acid, benzeneazo-β-naphthyl acetate yields aniline and α-amido-β-naphthol, mixed with a small quantity of a monacetyl-derivative of the base diamidohydroxynaphthyl-phenyl, $NH_2{\cdot}C_6H_4{\cdot}C_{10}H_5(OH^{\beta})(NH_2^{\alpha})$, the acetyl-group being most probably present in the α-amido-group in consequence of intramolecular transference in the ortho-position (Böttcher, *Berichte*, 1883, 1933). The triacetyl-derivative of the hydroxynaphthyl-phenyl base crystallises in white needles melting at 252°. If benzeneazo-β-naphthyl acetate be reduced in cold alcoholic solution with stannous chloride, the monacetyl-derivative of the hydroxynaphthyl-phenyl base is the chief product; but the instability of this compound does not allow of its being isolated. In a similar manner, it has been found that when boiled with tin and chlorhydric acid in alcoholic solution, benzeneazo-β-naphthyl benzoate gives aniline and α-amido-β-naphthol, the benzoyl being split off. α-Amido-β-naphthol and aniline are the chief products of mild reduction with stannous chloride, but the monobenzoyl-derivative of the naphthyl-phenyl base is also formed; the latter crystallises in white needles melting at 172—173°: the authors assign to it the formula $NH_2{\cdot}C_6H_4{\cdot}C_{10}H_5(OH^{\beta})(NH{\cdot}Bz^{\alpha})$, and suppose that the benzoyl is transferred to the amido-group as before by the intermediate formation of the anhydro-base. The diacetyl- and dibenzoyl-derivatives of α-amido-β-naphthol, $C_{10}H_6{<}^{NH{\cdot}C_2H_3O(\alpha)}_{O{\cdot}C_2H_3O(\beta)}$ and $C_{10}H_6{<}^{NH{\cdot}C_7H_5O(\alpha)}_{O{\cdot}C_7H_5O(\beta)}$, are also described. The first crystallises in colourless, rhombic prisms melting at 206°, and the second in whitish needles melting at 226·5°. The authors are engaged in investigating the products of reduction of the alkyl-derivatives of azo-β-naphthol compounds.

12. "The action of Nitric Acid on Anthracene." By A. G. Perkin.

Experiments on the preparation of nitro-derivatives of anthracene have up to the present failed, owing to the fact that when anthracene is treated with nitric acid, oxidation and nitration take place simultaneously, the products being anthraquinone and nitroanthraquinones. Nitro-derivatives of anthracene may, however, readily be prepared, provided that during the interaction of the anthracene and the nitric acid care is taken at once to decompose any nitrous acid which may be formed. If anthracene be gradually added to strong nitric acid (which has been carefully freed from nitrous compound by boiling it with urea), it is quickly converted into a new yellow substance, which after recrystallisation from coal-tar naphtha proved on analysis to be *dinitroanthracene*. This may also be prepared by the addition of anthracene to nitric acid diluted with nitrobenzene or the nitrates of the pyridine bases.

Dinitroanthracene crystallises in long, brilliant, yellow needles, which are difficultly soluble in the ordinary solvents. When carefully heated in a test-tube, it sublimes apparently without decomposition, but on long heating it is converted quantitatively into anthraquinone, with evolution of nitrous fumes, a proof that its constitution is represented by the formula $C_6H_4{\cdot}C_2(NO_2)_2{\cdot}C_6H_4$. The same change takes place when dinitroanthracene is oxidised with chromic acid, and also when it is exposed for some weeks to the action of sunlight.

Mononitroanthracene is contained, together with anthraquinone, in the mother-liquors from the preparation of dinitroanthracene. It crystallises from naphtha in small yellow needles, which are more readily soluble in this solvent than dinitroanthracene, but not so soluble as anthraquinone.

Diamidoanthracene is readily obtained by adding dinitroanthracene to a boiling solution of sodium sulphide in alcohol, and precipitating the resulting violet solution with chlorhydric acid. The orange powder thus produced is dissolved in hot alcohol, a little potash is added, and the solution allowed to cool. In this way beautiful silky, orange needles are obtained, which on analysis give numbers agreeing with those required for the formula $C_{14}H_8(NH_2)_2$. Diamidoanthracene is readily soluble in benzene and carbon bisulphide, less soluble in alcohol. It melts at 146°, and on oxidation with chromic acid yields anthraquinone.

The author is engaged in the further investigation of these substances.

13. "The preparation of Glyceric Acid." By T. Lewkowitsch, Ph.D.

Debus (*Annalen*, **106**, 79) and Sokoloff (*Annalen*, **106**, 85) recommend preparing glyceric acid from its repeatedly recrystallised calcium salt by means of the requisite quantity of oxalic acid; Mulder (*Ber.*, **13**, 1902), however, has proposed the use of lead glycerate and its treatment with sulphuretted hydrogen.

When recently preparing a quantity of glyceric acid, the author has found that it is impossible to completely convert the lead salt in the way indicated by Mulder, part of the lead remaining dissolved. A great number of experiments, carried out under various conditions, led all to the same result.

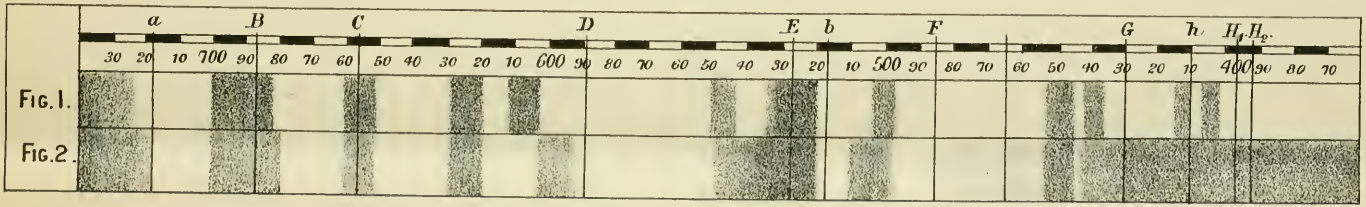
It is therefore necessary to return to the old prescription of Debus and Sokoloff, viz., to prepare glyceric acid from its calcium salt by means of oxalic acid.

14. "The relation of Cobalt to Iron as indicated by absorption-spectra." By W. J. Russell, Ph.D., F.R.S., and W. J. Orsman, Junr.

It is well known that when examined spectroscopically, some coloured metallic compounds are found only to produce a general absorption, but from previous observations it seemed possible to the authors that in some cases at least this might be resolved into bands by employing more powerful chemical agents than are generally used in such cases; experience had indicated that the chloride is usually the most suitable salt, and that it should be dissolved in chlorhydric acid and the liquid saturated with hydrogen chloride, also that, if possible, ether should be taken as solvent.

Applying these views to iron, it was found that ferric chloride gave a banded spectrum strikingly similar to that of cobalt chloride. Irons of all kinds were examined: pig iron, commercial cast iron, and various manufactured articles; steel in the form of wire, needles, and knives; and a number of specimens of reputed pure iron, viz., Demidorff's sheet iron, a sample of which was kindly given to the authors by Mr. Crookes, electro-deposited iron, and some ancient Indian iron from Professor Roberts Austen, and iron prepared by the late Dr. Matthiessen. Also a large number of iron ores—hæmatite Elba ore, Welsh bog ore, micaceous ore, ordinary spathic ore, a spathic ore found in cryolite, for which the authors have to thank Dr. Müller; Giderite, pyrites from the chalk, wolfram and rouge. Iron was also separated from the ignited residue of blood. All the specimens examined gave the same result.

Fig. 1 represents the bands seen in a solution of cobalt chloride to



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a scale of wave-lengths; the three most refrangible bands are easily photographed, but are not visible to the eye under ordinary conditions. The iron spectrum (Fig. 2) in general appearance closely resembles the cobalt spectrum, but the band which in cobalt is at 605 is slightly shifted nearer the blue, as shown in the diagram; there appears also to be a shift in the 501 band, but in the opposite direction. It was found that ether always dissolved out of the ferric chloride a substance which gave a band of extraordinary intensity exactly agreeing in position with the 530 band in the cobalt spectrum; further, that on increasing the strength of the ethereal solution, other bands became visible, agreeing with the bands observed in the strong chlorhydric solution of ferric chloride, and differing only in the case of the 690 and 655 bands, which in the ethereal solution were nearer the blue. Fig. 2 is the spectrum observed in a solution of iron in chlorhydric acid, peroxidised by any ordinary means.

For a variety of reasons the authors believe that this spectrum (Fig. 2) does not arise from the presence of cobalt in the iron. In the first place there is a constant difference between the two spectra, as shown in the position and appearance of the band at 597. A trace of cobalt dissolved along with the iron, gives the same spectrum as pure cobalt dissolved in chlorhydric acid. Again, on gradually increasing the strength of a pure cobalt chloride solution, the bands in the red are the first to appear, and the band at 530 is not visible until the general absorption has crept up as far as 580, completely blocking up the red end of the spectrum; in an ethereal solution from iron, on the contrary, this 530 band is the first to appear, and the bands in the red only become visible in comparatively strong solutions. Ether extracts the band-giving substance from the ferric chloride with great ease; but it abstracts nothing from the cobalt chloride. Again, on dissolving iron in chlorhydric acid, no bands are visible, and so long as the iron is in the ferrous state even ether extracts no band-giving substance; but on converting the ferrous into ferric chloride by nitric acid, or potassium chlorate, &c., the band-yielding substance is at once apparent. A known weight of Mr. Crookes's Demidorff iron was converted into chloride and dissolved in a known volume of ether, and the intensity of the bands compared with those given by cobalt chloride dissolved in a similar bulk of chlorhydric acid; it was found that approximately it required a weight of cobalt equal to that of the iron to give bands of similar intensity.

Discussion.

Mr. J. Norman Lockyer said that some years since, in a paper communicated to the Royal Society, he had suggested that there were

many different molecular groupings of the same element possible, and that spectrum analysis would disclose these; if the same molecular grouping were demonstrated in several substances, then undoubtedly there was a common constituent. If the bands described by the authors represent a substance common to iron and cobalt, it should be possible to obtain spectroscopic evidence of its presence at some temperature on volatilising the metals; although he had not fully studied cobalt and nickel comparatively, he had, in fact, found that under certain special conditions some of the spectroscopic appearances were common to both and in such a marked degree as to render it improbable that they were caused by impurities.

Dr. Perkin referred to the non-appearance of bands in an alcoholic solution of purpurin and their appearance in an ethereal solution, as an illustration of the influence of the solvent.

Dr. Armstrong remarked that the slight shift of the bands which had been referred to did not necessarily indicate that different substances were primarily the cause of the absorptions, as it was well known that such effects were observed on employing different solvents; the absorbing substance might in the one case be held in combination more firmly than in the other; this view was in harmony with the statement that ether did not extract the band-yielding substance in all cases.

Dr. Russell in reply said that not the spectrum as a whole, but only one of the bands was shifted. His view was that the solvents had broken up the substance into a finer state.

15. "Note on Methyl Fluoride." By Norman Collie, Ph.D.

MM. Moissan and Meslans have recently described (*Compt. rend.*, Dec. 31st, 1888) a new method of preparing methyl fluoride; but they do not seem to be aware that this substance had already been obtained in a state of purity (Lawson and Collie, *Chem. Soc. Trans.*, 1888, 626); the opportunity is therefore now taken to describe further experiments made with the gas.

The measurements of some of the physical constants of methyl fluoride have been made in conjunction with Professor Ramsay. The vapour-pressures taken at temperatures varying from -5° C. to 45° C. are as follows:—

Temp.	Press.	Temp.	Press.	Temp.	Press.
	mm.		mm.		mm.
−5° C.	11365	15° C.	23003	35° C.	36204
0	14696	20	25621	40	40196
5	17740	25	28840	45	46010
10	20091	30	32756	—	—

The substance assumes the critical state at 44·9° C. and at a pressure of 47123 mm. This pressure is probably slightly too high, owing to a trace of air, and the temperature too low. The error in pressure probably does not exceed 1500 mm., and of temperature 0·2° C.

A determination of the relative density of the gas gave 17·38, the theoretical number being 17·05. On exposing a mixture of equal volumes of methyl fluoride and chlorine to sunlight, it became colourless in a few hours, the interaction being $CH_3F + Cl_2 = CH_2ClF + HCl$. The further action of chlorine was found to take place much more slowly, and attempts to prepare CCl_3F were without success.

Discussion.

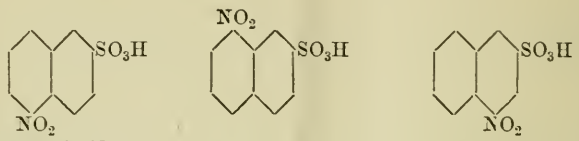
Professor Thorpe, after remarking on the importance of Moissan's researches on fluorine and its compounds, said that he feared that our Continental colleagues were less prone to take note of our work than we were of theirs. Moissan was generally said to be the discoverer of phosphorus trifluoride and oxyfluoride, but as a matter of strict history the former was first described by J. MacIvor, in the *Chemical News* (1875, **32**, 232), and the latter by Schulze (*J. pr. Chem.*, 1880, **21**, 442).

Dr. Collie said that he had incidentally described the preparation of methyl fluoride in a paper on the action of heat on tetramethylammonium compounds, and it was therefore not remarkable that his method had remained unnoticed by Moissan.

16. "The nitration of Naphthalene-β-Sulphonic Acid." By Henry E. Armstrong and W. P. Wynne.

According to Cleve, *three* isomeric α-nitro-β-sulphonic acids are produced on nitrating naphthalene-β-sulphonic acid; the chlorides of these acids melt respectively at 169°, 140°, and 125°. The sulphochloride melting at 125° corresponds to η-dichloronaphthalene (m. p. 48°); the remaining two were originally supposed by Cleve to furnish one and the same dichloronaphthalene melting at 61°, but subsequently he considered it probable that two distinct dichloronaphthalenes were formed, which melted at the same temperature, and this conclusion

would appear to receive support from the authors' discovery that there are two which melt at nearly the same temperature, viz., 1 : 3 $C_{10}H_6Cl_2$ (m. p. 61·5°) and 1 : 2′ or 1 : 3′ $C_{10}H_6Cl_2$ (m. p. 63·5°). In a recent paper (*Ber.*, 1888, 3275 Cleve has provisionally represented the three acids in question by the following formulæ, which had, however, previously been made known in Reverdin and Nölting's monograph :—



Sulphochloride : M. p. 125°. M. p. 140°. M. p. 169°.

A variety of considerations have led the authors to attempt the preparation of these acids : in the first instance they became specially interested in them on account of the supposed occurrence of isomeric change on treating two of them with PCl_5; then when it was discovered that two dichloronaphthalenes existed which melted at nearly the same temperature, corresponding, it was to be presumed, to two of the acids, it became of importance to ascertain which of the acids corresponded to the one and which to the other dichloronaphthalene, as their constitution would thereby be determined ; and lastly because, in the event of one of the acids being found to yield 1 : 3 dichloronaphthalene, the direct production of meta-derivatives of naphthalene would be established, a result of considerable theoretical importance, inasmuch as hitherto it has always been found that a heteronucleal α-derivative is formed in cases in which the corresponding benzene-derivative would afford a meta-derivative.

The authors have nitrated potassium naphthalene-β-sulphonate by grinding it up with 2·5 mol. proportions of nitric acid (1·5), and then heating on the water-bath; as soon as dissolution was effected, water was added, and the solution evaporated on the water-bath, water being frequently added. A partial separation of the isomeric acids by means of the barium salts was first effected in the manner recommended by Cleve; the various fractions were subsequently treated with PCl_5, and the sulphochlorides crystallised alternately from benzene, acetic acid, and carbon bisulphide. It was found that the nitration was complete. Both on account of the large proportion of the chloride melting at 169° which is obtained, and of its high melting point, the authors were led to expect that this compound would prove to correspond to the heteronucleal dichloronaphthalene melting at 63·5°, rather than to the 1 : 3-derivative as indicated by Cleve's formula, and they actually find this to be the case; on heating

the sulphochloride with PCl_5 at 220°, then steam distilling, resteaming the product, and crystallising it from alcohol, a dichloronaphthalene was obtained which melted at 62·5—63°; the sulphonic acid prepared therefrom gave an anhydrous potassium salt, and a sulphochloride which soon after its separation, when only partially opaque, melted at 115°, but subsequently when entirely opaque at 117·5°. Cleve's two nitrosulphochlorides, melting at 125° and 169°, therefore correspond respectively to the Dahl and Badische modifications of beta-naphthylaminesulphonic acid.

All attempts to separate a third sulphochloride have been unattended with success: products of intermediate melting point have indeed been obtained, but on recrystallisation have been resolved into the two chlorides melting at 125° and 169°. This result is perhaps significant, if the theoretical improbability of the formation of a meta-compound be borne in mind; but the authors are loth to accept the apparently logical interpretation of their results, as they are unacquainted with the precise conditions under which Cleve worked—only a very brief statement of his method having been made public—especially as the third acid is said by Cleve to be sparingly produced, and as it is within their own experience that slight variations in treatment, such as may escape notice, may materially affect the result. It is, however, noteworthy that Palmaer (*Ber.*, 1888, 3260) has obtained only the two heteronucleal β-sulphonic acids on sulphonating α-nitronaphthalene. In view of the importance of the question raised, it is hoped that Cleve will ere long communicate a detailed account of his method which will make it easy to verify his conclusions.

17. "The action of Bromine and Chlorine on the salts of Tetrethylphosphonium." By Orme Masson, M.A., D.Sc. (Edin.), and J. B. Kirkland, the University of Melbourne.

An account is given of experiments in continuation of those on the action of halogens on the salts of organic bases by Dobbin and Masson (*Chem. Soc. Trans.*, 1885 and 1886). The results show a very close general similarity between the polyhaloid-derivatives of tetrethylphosphonium and those of trimethylsulphine and of tetramethylammonium, previously described. The tendency to form solid polyhaloid compounds is, however, more marked. Thus, for instance, a crystalline tetrethylphosphonium tribromide, PEt_4Br_3, was obtained, whereas the previously described tribromides were unstable liquids; also a solid, but unstable, more highly brominated bromide, which was shown by synthetic experiments to have the composition PEt_4Br_7. Chlorine acting on the chloride gives only one compound, the trichloride, PEt_4Cl_3; but with the iodide it forms the tetrachloride,

PEt_4ICl_4, which is converted by alcohol into the dichloriodide, PEt_4ICl_2. Quantitative synthetic experiments were made to ascertain whether the sulphate really resembles the haloid compounds; from these it appears that it closely resembles the bromide in its behaviour towards bromine and the chloride in its behaviour towards chlorine, both in the nature and appearance of the products and in their composition. The solid brominated sulphate, $(PEt_4)_2SO_4{\cdot}Br_{12}$, yields the tribromide, PEt_4Br_3, when treated with alcohol. The most highly brominated derivative of the sulphate that could be obtained had the composition $(PEt_4)_2SO_4{\cdot}Br_{22}$; but it is doubtful whether this really represents a definite compound. The following table contains a list of the new substances, the methods of forming them, and their most marked properties. The first formula is queried because the experimental evidence does not suffice to establish it, though analogy renders it probable. The eighth formula is queried because of the doubt already expressed as to the definite nature of the substance to which it is assigned.

No.	Substance.	Method of formation.	Temp. of formation.	Chief properties.
1..	PEt_4IBr_4 (?).....	Br_2 on iodide.....	cold	Bright red crystal, solid, unstable.
2 .	PEt_4IBr_2	Alcohol on 1.....	—	Orange crystals: stable.
3..	PEt_4ICl_4	Cl_2 on iodide	70°	Yellow crystal mass: unstable.
4..	PEt_4ICl_2	Alcohol on 3.....	—	Yellow crystals, stable.
5..	PEt_4Br_7.....	Br_2 on bromide....	110°	Scarlet crystal mass: unstable.
6..	PEt_4Br_3.....	Alcohol on 5 or 9..	—	Red crystals: stable.
7..	PEt_4Cl_3	Cl_2 on chloride....	110°	Yellow crystal mass: unstable.
8..	$(PEt_4)_2SO_4Br_{22}$ (?).	Br_2 on sulphate ...	cold	Red liquid: unstable.
9..	$(PEt_4)_2SO_4Br_{12}$ ...	Br_2 on sulphate....	110°	Red solid: unstable.
10..	$(PEt_4)_2SO_4Cl_4$	Cl_2 on sulphate....	130	Yellow solid: unstable.

18. "The preparation of the salts of Triethylsulphine, Tetrethylphosphonium, and analogous bases." By Orme Masson, M.A., D.Sc. (Edin.), and J. B. Kirkland, University of Melbourne.

When sulphur is heated with ethyl iodide in sealed tubes at 180°, it entirely disappears and is converted into triethylsulphinetriiodide, $S + 3EtI = SEt_3I_3$; on treating this triiodide under water with hydrogen sulphide it is converted into the iodide, from which the hydroxide, &c., may be prepared. The yield is nearly a theoretical one.

The same process is applicable to the preparation of selenine salts from selenium, and of tetraethylphosphonium salts from phosphorus—either the ordinary or the red modification. In the case of phosphorus, however, a mixture of two different polyiodides is obtained: $2P + 7EtI = PEt_4I_3 + PEt_3I_4$. The second of these is converted by the treatment with hydrogen sulphide and water into triethylphosphine oxide, so that only half of the phosphorus goes to form the phosphonium salt, $PEt_4I_3 + H_2S = PEt_4I + 2HI + S$; $PEt_3I_4 + H_2S + H_2O = PEt_3O + 4HI + S$. The yield obtained is very nearly theoretical.

The use of silver hydroxide may be obviated by adopting Hofmann's potash process in recovering tetrethylphosphonium iodide from the solution obtained after the hydrogen sulphide treatment. The solution is saturated with potash and warmed, when the iodide forms an oily layer on the surface, which is readily separated and purified. This method works well, and it also answers in the case of the sulphine preparation.

The researches of Carius and of Crafts and Silva on the preparation of triethylphosphine oxide from phosphorus and ethyl iodide are criticised in the light of the results of the present investigation.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Smithsonian Miscellaneous Collections: 663, Index to the Literature of Columbium, by F. W. Traphagen. Washington, 1888.
From the Institution.

Rapport fait au comité des stations agronomiques et des laboratoires agricoles, par la sous-commission des methodes analytiques. Nancy 1888. From Mr. Warington.

II. *By Purchase.*

La margarine et le beurre artificiel, par C. Girard et J. De Brevans. Paris 1889.

Die chemische und mikroskopisch-bacteriologische Untersuchung des Wassers, von F. Tiemann und A. Gärtner. Erste Lieferung, Braunschwig 1889.

Hülfstabellen zur mikroskopischen Mineral-Bestimmung in Gesteinen, von H. Rosenbusch. Stuttgart 1888.

At the next meeting on February 21st, there will be a ballot for election of Fellows, and the following papers will be read :—

"The density of gaseous hydrogen fluoride." By Professor Thorpe and F. J. Hambly.

"Note on the decomposition of potassic chloride by heat in the presence of manganic peroxide." By Professor McLeod.

"Contributions to the chemistry of lignification." By C. F. Cross and E. J. Bevan.

"Determination of the atomic weight of chromium." By S. G. Rawson.

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Issued 28/2/1889.

ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 63. Session 1888-89.

February 21st, 1889. Mr. W. Crookes, F.R.S., President, in the Chair.

Mr. A. E. Tutton was formally admitted a Fellow of the Society.

It was announced that the following changes in the Council List were proposed by the Council :—

As *President*, Dr. W. J. Russell, F.R.S., *vice* Mr. Crookes, F.R.S.

As *Vice-Presidents*, Professor J. Emerson Reynolds, F.R.S., and Mr. R. Warington, F.R.S., *vice* Mr. Howard and Prof. Schorlemmer.

As *Members of Council*, Dr. N. Collie, Prof. J. Ferguson, M.A., Mr. S. U. Pickering, M.A., and Mr. J. F. M. Page, *vice* Profs. Carnelley, P. F. Frankland and Ramsay, F.R.S., and Mr. Friswell.

Messrs. R. H. Davies, R. J. Friswell and S. Rideal were appointed by the meeting to audit the Treasurer's accounts.

Certificates were read for the first time in favour of Messrs. John Leigh Hoskyns-Abrahall, Norman Villa, Rusholme, Manchester; James Annal, 3, Reid Street, Dundee; Richard Douglas Bailey, City Brewery, Gloucester; Henry Richardson Hoyles, c/o Messrs. Thacher & Co., Bombay; Clement Joseph Leaper, 4, Chester Road, Ranelagh, Dublin; George T. Wilkinson Newsholme, 74, Market Place, Sheffield; Richard W. Roberts, 22, Calle Arturo Prat, Valparaiso, Chili; Thomas Alexander Shegog, 39, St. Mary's Road, Dublin; Henry Simmons, 9, Christ Church Terrace, Cheltenham; Patrick Alexander Weir, M.B., Ghazipur, N.W.P., India; Charles Wood, 5, Woodview, Bradford, Yorks.

The following were elected Fellows of the Society :—Messrs. P. Carmody, Edward Mitchell Chaplin, John W. Clayton, John Curragh, Philip Norman Evans, Robert Ferguson, M.A., David Ferrier, Conrad Gerling, Alfred Miall Hanson, John Joseph Hickey,

William H. Jowett, William E. Lauer, George McCalman, Harry East Miller, Arthur F. Morgan, Henry Joshua Phillips, George Arthur Pingstone, Harry Hollis Robins, Stanley Southam, James Speakman, Thomas B. Stillman, George Sherbrooke Turpin, M.A., B.Sc., Thomas John Underhill.

The following papers were read :—

19. "Note on the decomposition of Potassic Chlorate by heat in the presence of Manganic Peroxide."

Having observed the alteration in appearance that peroxide of manganese undergoes when heated with potassic chlorate, the author has made a number of experiments, using different kinds of oxide of manganese, determining the loss of weight that the mixture suffers when heated and also the quantity of chlorine simultaneously generated. The heating was generally effected by the vapour of boiling mercury, at which temperature the potassic chlorate is not changed. The more finely divided the peroxide, the more rapid is the action and the more chlorine is evolved. When the evolution of chlorine is prevented by the addition of a small quantity of sodic or potassic carbonate, the decomposition of the chlorate proceeds very slowly, unless the temperature be raised much above that of boiling mercury. When potassic chlorate is fused with a minute quantity of peroxide of manganese, the residue is found to be pink on cooling, indicating the presence of a permanganate: and inasmuch as potassic permanganate is decomposed at a temperature of 275°, it is not improbable that the permanganate is decomposed by the heat as rapidly as it is produced into potassic manganate, manganic peroxide, and oxygen; the resulting potassic manganate is acted on by chlorine generated by the action of the peroxide on some fresh chlorate, forming potassic chloride, manganic peroxide and oxygen, so that the peroxide is being continually reproduced. The quantity of chlorine evolved corresponds to only a very small proportion of the manganic peroxide present, so if the first action really takes place, the chlorine must be absorbed and employed in converting the potassium into chloride.

Discussion.

Professor Thorpe, referring to the well-known fact that no perchlorate is formed in presence of manganese dioxide, asked how this was to be explained.

Mr. Williams stated that he had been unable to obtain the theoretical amount of oxygen from potassium chlorate by heating it *in vacuo*: a gas was given off which attacked mercury—presumably

chlorine, and therefore it was probable that the residue contained potassium peroxide. On heating silver iodate *in vacuo* the theoretical amount of oxygen was obtained without difficulty.

Professor McLeod said that he was unable to account for the non-production of perchlorate in presence of manganese dioxide; as potassium perchlorate was not decomposed by heating with manganese dioxide, it probably was not even an ephemeral product. He had without difficulty obtained almost the theoretical amount of oxygen from chlorate. He did not think that the pink colour was due to ferrate as had been suggested, as he had found that iron oxide gave a somewhat different colour.

Professor Ramsay remarked that Stas, in his determination of the ratio of potassium chloride to oxygen in chlorate, had not found that peroxide was formed.

20. "The vapour-density of Hydrogen Fluoride." By T. E. Thorpe, F.R.S., and F. J. Hambly.

Gaseous hydrogen fluoride, on being heated from a few degrees above the boiling point of the liquid, shows a rapid decrease in density, owing to the dissociation of H_xF_x molecules ultimately into HF molecules, the course of the dissociation being similar to that observed in the case of nitrogen peroxide and acetic acid. The authors have carefully studied the molecular breaking down of the vapour as it is effected by changes of temperature and pressure. It would appear that there is no evidence for the existence of a molecule corresponding to the formula H_2F_2. If it exists at all, it must be formed only during the process of transition of H_xF_x into xHF, and be such that it can persist under given circumstances only in the presence of definite proportions of molecules more or less complex than itself. The density at above 32° corresponds apparently with H_2F_2, but the curve gives no indication of any condition of statical equilibrium in the neighbourhood of this temperature such as would be manifest if such a molecule were capable of independent existence. At temperatures below this point the density gradually increases in a perfectly regular manner until at 26·4°, the lowest temperature observed, the density becomes 1·773, equivalent to a molecular weight of 51·2 ($H_3F_3 = 60$); as it is heated the vapour behaves like a mixture of a complex molecule H_xF_x, or of H_xF_x and H_yF_y molecules. with a gradually increasing number of molecules of HF, the process of dissociation being perfectly continuous until the temperature increases to about 60°, when the density becomes approximately normal, *i.e.*, corresponds to a vapour consisting wholly of HF molecules.

As in the case of nitrogen peroxide, dissociation takes place with increasing rapidity as the temperature increases until it attains a maximum when about 50 per cent. of the heavier molecules have been decomposed, after which the increase becomes gradually smaller, at first slowly, then rapidly. The curves showing the mean increase resemble in fact that given by Naumann (*Thermochemie*, 1882) as representing the increase in the rate of dissociation of nitrogen peroxide, but with this very marked difference, that the mean increase for 1° C. in the case of hydrogen fluoride is at its maximum nearly three times as great as that of nitrogen peroxide.

The authors have studied the effect of pressure on the course of the dissociation by attenuating a given volume of the gas maintained at the constant temperature of 32°, at which point the vapour is supposed to consist wholly of H_2F_2 molecules. It is seen that the slightest alteration of pressure at this temperature at once disturbs the ultimate proportion of the complex to the simpler molecules in the gaseous mixture—a fact which again points to the non-existence of a stable molecule corresponding to H_2F_2. The reduction of the actual pressure may be effected not only by direct attenuation but by mixing the vapour with a neutral gas. Experiments made by the addition of dry air showed that the intervention of the air particles has no effect on the extent of the ultimate decomposition of the complex hydrogen fluoride molecules corresponding to a particular diminution of pressure. The presence of the air may alter the rate of the dissociation, but it has no appreciable influence on its maximum amount. Lastly, they see in the fact that their values for the density at *circa* 32°, under ordinary atmospheric pressure, agree almost exactly with those obtained by Mallet, a proof that the nature of the vessel or the character of its surface exert no appreciable effect on the extent of the dissociative change, Mallet's experiments having been made in glass coated with paraffin, whereas those of the authors were made in a vessel of platinum. This point is of importance in view of Konowalow's experiments on the effect of surface in influencing the rate and extent of dissociation.

Discussion.

Professor Ramsay said that Professor Thorpe, in speaking of the analogy of the results obtained in the case of hydrogen fluoride with those of the Brothers Natanson for nitric peroxide, had pointed out that these latter afforded insufficient proof of the higher limiting value of n in the formula N_nO_{2n}; and that this limiting value was also unknown in the case of acetic acid, of which the vapour-density also increased with fall of temperature. Now there were three separate lines of argument leading to a knowledge of the higher limiting

formulæ of these bodies which had been pointed out by himself and Dr. Young, and of which the data were to be found in papers publishe l in the *Philosophical Transactions*, in the *Philosophical Magazine* and in the *Chemical Society's Transactions*. The first of these has reference to the alteration of density of the saturated vapour with fall of temperature and corresponding fall of pressure. It is argued that the density of the vapour of a substance must necessarily, at any given temperature, be higher when the vapour is on the point of condensation than when it is unsaturated. Hence, if it can be proved that the density of the saturated vapour of bodies like nitric peroxide and acetic acid shows no signs of increasing beyond those required for the respective formulæ N_2O_4 and $C_4H_8O_4$, such formulæ must denote the limit of complexity of the molecules, in the gaseous state at least. To ascertain such a limit, Dr. Young and the speaker constructed from the Natansons' data for the relations of volume, pressure and temperature of nitric peroxide, and their own data for the vapour-pressure of of that body, isothermal curves in which pressures formed ordinates and vapour-densities abscissæ. The terminal points of such curves are characterised by rapid increase of density without rise of pressure, and, in fact, denote that the substance is no longer in the gaseous state, the vapour-pressure of the liquid having been reached. The densities of the saturated vapour therefore will correspond with the angles of union of the isothermal curves with horizontal straight lines representing condensation to liquid under vapour-pressures constant for each temperature. By joining with each other such angles of union for each temperature a curve is obtained expressing the densities of the *saturated* vapour in relation to pressure. It is evident from inspection of such a curve for acetic acid, shown in a plate in the *Society's Transactions* (1886, 806), that the line of zero-pressure would be cut at the density 60, corresponding to the formula $C_4H_8O_4$; a similar curve can be constructed from the Natansons' results and Ramsay and Young's determinations of the vapour-pressures of nitric peroxide, and this intersects the line of zero-pressure at a point corresponding to the vapour-density 92, equivalent to the formula N_2O_4.

The second argument is as follows: Representing the relations of temperature and pressure of a "perfect" gas for any given constant volume, $p = c \,.\, t$, where c is a constant and t absolute temperature. This is the equation to a straight line; such a line is termed an *isochoric line* or *isochor;* its point of origin for a perfect gas is absolute zero of pressure and temperature. If a different volume be chosen, the slope of the line is different. Now it is clear that if a given volume of gas contains $2n$ mols., pressure will rise with rise of temperature at twice the rate that it would if the given volume of

gas contained n molecules. Constructing for nitric peroxide and for acetic acid, on the assumption that they are perfect gases, diagrams showing the relations of pressure and temperature for the formulæ NO_2 and $C_2H_4O_2$ at such volumes that 1 gram occupies, say, 1000 cubic centimetres in each case, the resulting straight lines will manifestly differ in slope from those corresponding to the respective formulæ N_2O_4 and $C_2H_8O_4$, the pressure in the latter case not rising so rapidly with rise of temperature, owing to the smaller number of molecules in that volume. But we know that the actual behaviour of these bodies is not that of perfect gases. The line representing the relations of pressure and temperature should at high temperatures, when the substances exist in the molecular state NO_2 and $C_2H_4O_2$, nearly coincide with the theoretical line for these molecular states; and at low pressures and temperatures with the line denoting the molecular condition N_2O_4 and $C_4H_8O_4$. The data of actual experiments show that such is the case. The S-shaped isochoric curve trends so that it is probable that it would become tangential with that expressing the behaviour of molecules of the higher formulæ, showing no signs of cutting it, as it must needs do, were still more complex molecules capable of existence.

The third line of argument is derived from the application of Raoult's method to a solution of nitric peroxide in acetic acid; the results obtained by the speaker show that even with very varying proportions of peroxide the molecular weight corresponds closely with the formula N_2O_4.

In conclusion, Prof. Ramsay suggested that it was very desirable that the authors should, if possible, obtain data for a greater number of isothermals than the two which they had already constructed, so as to afford means for determining the true complexity of the molecule; and also that such results should be checked by the application of Raoult's method, dissolving the hydrogen fluoride in glacial acetic acid.

Professor Thorpe said that it was impossible to apply Raoult's method, on account of the violence of the action which took place on adding hydrogen fluoride to acetic acid.

21. "Contributions to the Chemistry of Lignification; the constitution of the Jute Fibre Substance." By C. F. Cross and E. J. Bevan.

The authors describe the results of fuller study of the ligno-celluloses (compare *Chem. Soc. Trans.*, 1882, 90; 1883, 18). The substance of the jute fibre may be empirically represented by the formula $C_{12}H_{18}O_9$, and although an aggregate, its properties and com-

position are sufficiently constant to warrant its being regarded as a chemical unit. It is to a certain extent attacked and dissolved by hydrolytic agents, but the insoluble residues possess the composition and properties of the original; hydrolytic agents which are at the same time oxidising agents, *e.g.*, dilute nitric acid, however, cause its resolution into insoluble cellulose and soluble non-cellulosic acid products. On treatment with a mixture of concentrated nitric and sulphuric acids, it is converted into explosive nitrates, ultimately into what appears to be the tetranitrate, $C_{12}H_{14}O_5(NO_3)_4$.

The characteristic action of chlorine, whereby ligno-cellulose is resolved into cellulose and a yellow chlorinated derivative, has been studied by a special method and apparatus, and it is shown that interaction takes place according to the equation $C_{456}H_{702}O_{342} + 24Cl_2 = 6C_{19}H_{17}Cl_4O_9 + 57C_6H_{10}O_5 + 3H_2O + 24HCl$. Previous observations showed the probable presence in the chlorinated fibre of mairogallol.

A comparison of the composition of the latter with that of the chlorinated derivative, however, indicates that it is associated with another substance having approximately the formula $C_{137}H_{169}O_{59}$.

Moreover, the chlorinated derivative has been found to contain a constituent yielding on hydrolysis furfural and acetic acid. These compounds are also readily yielded by the original ligno-cellulose, and the quantities obtained confirm the empirical formula deduced as above from the statistical comparison with mairogallol.

The non-cellulosic constituent therefore appears to be composed of (*a*) a group, $C_{18}H_{18}O_{10}$—a ketone transitional to a quinone, capable of combining directly with chlorine to form mairogallol; (*b*) a furfural group, $C_5H_4O_2$, in combination by condensation with *a* and with (*c*), a group yielding acetic acid. These are associated in the approximate molecular proportions of (*a*) 2, (*b*) 6, (*c*) 5 = $C_{76}H_{80}O_{37}$.

From the examination of various types of lignified tissues and fibres, the authors conclude that the composition of the ligno-celluloses in the earlier stages of growth approximates to that of jute; but that in the true woods, in which the carbon percentage is higher and the properties of which differ sensibly from those of the first named—condensation has proceeded further.

22. "The atomic weight of Chromium." By S. G. Rawson, B.Sc.

The author has determined the equivalent of chromium by converting a known weight of carefully purified ammonium bichromate into chromic oxide: the chromate was first reduced by means of alcohol and muriatic acid, an excess of ammonia solution was then added to precipitate the chromium as hydroxide, the water was removed by

evaporation, and after drying the residue at 140°, the ammonium salt was expelled by ignition in a muffle. All the operations were carried out in one and the same platinum dish; full details are given in the paper. The following are the results obtained:—

Weight of $(NH_4)_2Cr_2O_7$ (corrected).	Weight of Cr_2O_3 (corrected).	Ratio of Cr : H.
1·01275	0·61134	52·130
1·081806	0·65266	52·010
1·29430	0·78090	52·020
1·13966	0·68799	52·129
0·98778	0·59595	52·016
1·14319	0·68987	52·059
	General mean	52·061
	Maximum difference.	0·120

At the next meeting on March 7th, there will be a ballot for the election of Fellows, and the following papers will be read:—

"The constitution of certain Naphthalene-derivatives." By Dr. Armstrong and Mr. Wynne.

"The decomposition of Carbon Bisulphide by shock." By Professor Thorpe.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 64. Session 1888–89.

March 7th, 1889. Mr. W. Crookes, F.R.S., President, in the Chair.

Messrs. P. Norman Evans, Percy A. E. Richards and Thomas J. Underhill were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Frederick William Boam, 2, De Montford Square, Leicester; William Frew, King James Place, Perth; James Hall, Grove House, Tottenham; James Bruce Miller, Rubislaw, Den North, Aberdeen; George Cannon McMurtry, 35, Binfield Road, Clapham, S.W.; John Charles Platts, 25, Harcourt Road, Crookesmoor, Sheffield; Duncan Taylor Richards, 12, Park Terrace, South Shields; John William Slater, 36, Wray Crescent, Tollington Park, N.; William John Waterhouse, 211, Lord Street, Southport; Mortimer Woolf, 3, Acoll Road, West Hampstead.

The following papers were read :—

23. "The decomposition of Carbon Disulphide by shock; a Lecture Experiment." By T. E. Thorpe, F.R.S.

The author, in studying the action of the fluid alloy of potassium and sodium on carbon disulphide, obtained a yellowish-brown solid substance which exploded with great violence when subjected to pressure or friction. If the explosion occurred in contact with carbon disulphide that substance was resolved into its elements.

As carbon disulphide is an endothermic compound, the author was induced to try whether its vapour could not be resolved into its elements by the explosion of various detonating agents, *e.g.*, mercuric fulminate, in the manner indicated by Berthelot. It is found that such a decomposition is readily effected by exploding a charge of 0·05 gram fulminate within a stout glass tube containing a few c.c. of carbon

disulphide vapour. The carbon disulphide is at once resolved into carbon and sulphur, which line the inside of the tube. The experiment may be easily made with perfect safety, and forms a good illustration, for class purposes, of the resolution of an endothermic substance into its elements by sudden shock.

Discussion.

The President pointed out that the spectrum of mercury was rich in ultra-violet rays, and suggested that perhaps the decomposition was induced by these rays.

Professor Thorpe, in reply, said that this explanation had not occurred to him; he believed, however, that the effect was purely mechanical, inasmuch as Berthelot had, in fact, exploded nitrous oxide by sudden compression. In reply to Mr. Groves, he said that he had only experimented with the gaseous disulphide; he believed that no explosive compound was formed by treating the disulphide with sodium.

24. "The determination of the constitution of the Heteronucleal $\alpha\beta$- and $\beta\beta$-di-derivatives of Naphthalene." By Henry E. Armstrong and W. P. Wynne.

In a recent communication (*Chem. Soc. Proceedings*, No. 58, 1888, p. 104) the authors have shown that proof has now been obtained that the two dichloronaphthalenes melting at 48° and 63·5°, corresponding respectively to the Dahl and Badische modifications of betanaphthylaminesulphonic acid, are the 1 : 2′ and 1 : 3′ *heteronucleal* dichloronaphthalenes; at the same time they have insisted that it is impossible from existing data to determine whether the compound melting at 48° is the 1 : 2′, and that melting at 63·5° the 1 : 3′-derivative or *vice versâ*, and this they have done notwithstanding the evidence brought forward by Erdmann and Kirchhoff (*Annalen*, 247, 366; *Berichte*, 1888, 3447; these *Proceedings*, No. 61, 1889, p. 8). These chemists have inferred that the dichloronaphthalene melting at 48° is the 1 : 3′-derivative, as they prepared it synthetically from metachlorobenzaldehyde; and they regard the isomeride which the authors have shown melts at 63·5° as the 1 : 2′-derivative, as they obtained it from parachlorobenzaldehyde. The authors have on several occasions criticised Erdmann and Kirchhoff's arguments and have pointed out their insufficiency, their main objection being that the position of the hydroxyl in the naphthol-derivatives prepared synthetically could not be determined; they have also suggested that in some cases the hydroxyl might take up the position indicated by Erdmann and Kirchhoff, and

in others the alternative alpha-position. Moreover it appears to them that the argument recently advanced by Erdmann (*Berichte*, 1888, 3447) in reply to their criticism, is deprived of its force by Erdmann's own admission that phenylisocrotonic acid is converted with exceptional ease into the corresponding lactone; however stable the lactone may be when formed, the fact that it is so readily producible is indicative of the manner in which the naphthol-hydroxyl might eventually assume a different position from that assigned to it by Erdmann. And even if no argument of this kind could be advanced, the fact that condensation is effected at a relatively high temperature and that it involves considerable molecular rearrangement, renders the occurrence of isomeric change both possible and probable.

Believing that, "as in the case of benzene there is little doubt that the constitution of naphthalene-derivatives will be determined eventually by the study of naphthalene-derivatives and not by synthetic methods of the character of those of Erdmann and Kirchhoff" (*Brit. Assoc. Rep.*, 1888; *Chem. News*, 58, 295), they have devoted their attention to the study of the chloronaphthylaminesulphonic acids: by determining the relative positions of the three pairs of radicles Cl and NH_2, Cl and SO_3H, and NH_2 and SO_3H in such acids it is obviously possible to determine the relative positions of the three radicles in a heteronuclcal chloramidosulphonic acid, and on this result the absolute orientation of the radicles may be based, *provided* that it can be shown how the radicles are situated in any one of the two pairs of hetero-di-derivatives obtainable from the tri-derivative. No absolute method, free from reproach, has yet been devised of determining the constitution of any known hetero-di-derivative of naphthalene, but in the case of the $\alpha\alpha$-compounds, arguments may be advanced which are of such weight as to leave but little room for doubt. The two possible hetero-$\alpha\alpha$-compounds are represented by the symbols

I.

II.

There can be little doubt, and it is indeed generally held, that so-called α-dinitronaphthalene (m. p. = 216°) and the corresponding γ-dichloronaphthalene (m. p. = 107°) are compounds of type I, and that β-dinitronaphthalene (m. p. 170°) and the corresponding ζ-dichloronaphthalene (m. p. = 83°) are compounds of type II. Thus β-diamidonaphthalene, according to Aguiar's observations on its

behaviour towards nitrous acid and towards oxalates (*Ber.*, 1874, 313), behaves in an altogether peculiar manner, simulating that of an ortho-di-derivative, as pointed out originally by Ladenburg (*ibid.*, 1878, 1651). The pseudortho-character of β-diamidonaphthalene and the corresponding di-derivatives is also established by Ekstrand's investigation of the nitronaphthoic acid corresponding to β-dinitronaphthalene (*ibid.*, 1883, 2881); by Bamberger's investigation of naphthalic acid (*ibid.*, 1887, 237); and by Erdmann's investigation of the α-amido-α-sulphonic acid obtained on reducing the so-called Schöllkopf α-nitronaphthalene-α-sulphonic acid (*Annalen*, **247**, 343). On the other hand, an argument of great force in favour of the adoption of a formula of type I for α-dinitronaphthalene and other corresponding uniform di-derivatives (derivatives containing two similar radicles) may be derived from the fact that all melt at higher temperatures than the isomeric αα-compounds; it is to be expected, on general grounds, that compounds of symmetrical structure would be thus distinguished.

By sulphonating 1 : 2 α-chloro-β-naphthylamine hydrochloride by means of four times its weight of an acid containing about 2 per cent. of SO_3, the authors have succeeded in obtaining three isomeric α-chloro-β-amidosulphonic acids. No. I acid is produced in largest amount and almost exclusively if sulphonation be effected by heating at 70° for six hours. If the heating be prolonged for about six hours at a somewhat higher temperature, viz., about 100°, No. II acid is the chief product. No. III acid is chiefly produced if sulphonation be effected by heating during about six hours at about 160°. No. I acid is very difficultly soluble in water; it is best purified by dissolving it as sodium salt in a large bulk of boiling hot water and precipitating by acid; the separated acid is at once filtered off, and these operations are several times repeated. It usually crystallises in glistening, flat, elongated prisms; its salts crystallise well, but are easily soluble, especially the sodium and ammonium salts. No. II acid is slightly more soluble than the No. I acid, and crystallises in a less characteristic manner; its salts are difficultly soluble; the sodium salt is especially characteristic, being almost insoluble in the presence of alkali: it crystallises with $4\frac{1}{2}$ mols. H_2O in glistening, apparently monoclinic plates. No. III acid is the most soluble, and yields very soluble salts, which do not crystallise well; it crystallises in tufts of needles. This acid is best separated from No. II acid by means of the ammonium or sodium salts.

In order to determine the constitution of these acids the authors have, on the one hand, displaced the halogen by means of sodium amalgam, and, on the other, have displaced the β-amido-group by means of v. Baeyer's hydrazine method. They have already ascer-

tained that the No. I acid affords the Dahl modification of betanaphthylaminesulphonic acid, and the No. III acid the so-called *ε*-acid of Bayer and Duisberg; the investigation of the amido-acid from No. II acid, and of the three chlorosulphonic acids derived from the three chloramidosulphonic acids is also almost completed.

In the number of the *Chemiker Zeitung* just to hand, mention is made of the title of a paper by P. Hellström, read at the Swedish Academy of Sciences on February 13th, from which it appears that the same subject is elsewhere being investigated, and it is on this ground alone that the authors are induced to communicate their results in the present incomplete form.

There is little doubt that under ordinary conditions of sulphonation chlorobetanaphthylamine will yield other products than those described, and in fact others have already been observed. The authors propose also to study the sulphonic acids obtained from other chloronaphthylamines, and have, in fact, already prepared acids from dichloralphanaphthylamine, from 1 : 2-chloralphanaphthylamine and from bromalphanaphthylamine. It is anticipated that in this way it will be possible to determine the constitution of the dichloronaphthalenesulphonic acids, and hence to determine the manner in which substitution is effected in their formation. From their No. 1 chloramidosulphonic acid the authors have already prepared the corresponding dichloronaphthalenesulphonic acid, and find that it is identical with the chief product of the sulphonation of the 1 : 2-dichloronaphthalene melting at 34°, that, namely, which yields a sulphochloride crystallising in massive prisms melting at about 105° (*Brit. Ass. Report*, 1888; *Chem. News*, **58**, 296).

25. "The action of Chloroform and Alcoholic Potash on Phenylhydrazine." By S. Ruhemann, Ph.D., M.A.

The author finds that together with the compound previously described by Mr. Elliott and himself (*Chem. Soc. Trans.*, 1888, 850), which he proposes to call *diisocyananilide*, there is formed a certain amount of formylphenylhydrazine, $C_6H_5{\cdot}NH{\cdot}NH{\cdot}COH$.

From formyl, in like manner, he has obtained formyltolylhydrazine and diisocyanparatoluidide; the latter crystallises in faintly yellow plates, melting at 185°.

Diisocyananilide is converted by the action of methyl iodide into a methammonium iodide of the formula $C_{14}H_{11}N_4(CH_3){\cdot}CH_3I$, the production of which is proof of the presence of an imido-group. On adding bromine to an acetic solution of the anilide, a mixture of a monobromo- (m. p. 220°) and a tribromo-derivative is precipitated; the solution containing a third substance (m. p. 131°) of the formula $C_{14}H_{10}Br_2N_4$.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

The American Chemist, a Monthly Journal of Theoretical, Analytical, and Technical Chemistry; edited by C. F. Chandler and H. Chandler. Vols. I—V (all that were issued). New York 1870–1875.
From Dr. Hugo Müller.

The Scientific Works of C. William Siemens, Kt.; edited by E. F. Bamber. Vol. I, Heat and Metallurgy; Vol. II, Electricity and Miscellaneous; Vol. III, Addresses, Lectures, &c. London 1889.
From the Executors of the late Sir William Siemens.

U. S. Geological Survey. Mineral Resources of the United States; Calendar Year 1887. By D. T. Day. Washington 1888.
From the Director of the Survey.

Analisi dell' acqua ferruginosa di Cavelonte di D. Leonardi. Trento 1867.

L'école des engrais chimiques, par Georges Ville, 2me édition. Paris 1869.

Les engrais chimiques. Entretiens agricoles donnés au champ d'expériences de Vincennes dans la saison de 1867, par Georges Ville. 2me édition. Paris 1868. From Walter White, Esq.

U. S. Treasury Department. Report of the Commissioner of Inland Revenue for the fiscal year ended June 30, 1888, by J. S. Miller. Washington 1888. From the Author.

Practical Organic Chemistry: the Detection and Properties of some of the more important Organic Compounds, by S. Rideal. London 1889. From the Publishers.

At the next meeting, on March 21st, the following papers will be read:—

"The Molecular Weights of Metals." By Prof. Ramsay, F.R.S.
"Compounds of Tribenzylphosphine Oxide." By Dr. Collie.
"The rate of Dissolution of Metals in Acids." By V. H. Veley.
"The Constitution of Primuline." By A. G. Green.

The Anniversary Meeting will be held on Thursday, March 28th, at 8 P.M. The President will deliver an address on "Recent Researches on the Rare Earths as interpreted by the Spectroscope."

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 65. Session 1888–89.

March 21st, 1889. Mr. W. Crookes, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. John Kitchen, Beech Grove, Ulverston; John Edmund Legg, Elm House, Great Berkhamstead, Herts; Walter J. Sykes, 47, Ouseley Road, Balham, S.W.; William Virtue, The Laboratory, Crosswells Brewery, Oldbury.

26. "The Molecular Weights of the Metals." Preliminary Notice. By William Ramsay, Ph.D., F.R.S.

The molecular weights of a number of metals have been determined by Raoult's vapour-pressure method, viz., by ascertaining the depression of the vapour-pressure of the solvent produced by a known weight of dissolved substance. The connexion between osmotic pressure and depression of vapour-pressure has been shown by van't Hoff, and in a recent number of the *Zeitschrift für physikalische Chemie* by Arrhenius; the method of the latter is characterised by great simplicity. It has also been mathematically developed by Planck (see also *Zeitschr. f. phys. Chem.*, 1888, 405).

The relation between molecular weight and depression is expressed by the equation

$$W = \frac{W' \times P \times p}{100 \times d},$$

where W is the molecular weight to be found; W′ the molecular weight of the solvent; P/100 the percentage weight of the dissolved substance in solution; p the vapour-pressure of the solution; and d the depression in the vapour-pressure of the solvent produced by adding the substance dissolved. It will be noticed that the relation is independent of temperature.

The solvent employed was liquid mercury; the temperatures 260° and 270° for a few substances, and the boiling point of mercury for

most. The apparatus, of which a description will appear in the complete paper, is of the simplest description, and lends itself to the determination of molecular weights of all substances soluble in any pure menstruum; no knowledge of the vapour-pressures of the solvent being required. The method is much more generally and easily applicable than the alternative method of Raoult whereby the molecular weight is deduced from the depression of the melting point of a solvent due to dissolved substance.

The results obtained are as follows:—

Element.	Atomic weight.	Molecular weight.		Molecular formula.
		Found.	Calculated.	
Lithium	7·02	7·00	7·02	Li_1.
Sodium	23·04	12·1	11·52	$Na_{\frac{1}{2}}$.
Potassium	39·14	28·57	?	K_1 ?.
Silver	107·93	109·0	107·93	Ag_1.
Gold	197·22	204·3	197·22	Au_1.
Barium	137·0	74·45	68·5	$Ba_{\frac{1}{2}}$.
Magnesium	24·3	20·33	24·3	Mg_1.
Zinc	65·34	60·85	65·43	Zn_1.
Cadmium	112·1	100·0	112·1	Cd_1.
Gallium	69·9	68·1	69·9	Ga_1.
Thallium	204·2	183·5	204·2	Tl_1 (?).
Tin	119·1	114·9	119·1	Sn_1.
Lead	206·93	204·1	206·9	Pb_1.
Antimony	120·2	134·2	120·3	Sb_1.
Bismuth	208·1	209·2	208·1	Bi_1.

These numbers represent some of the actual results. Nevertheless, they must not be taken as absolute; although in many cases they are conclusive as to the molecular weight of the metal, still further experiments are needed. As an instance of what occurs, the metals thallium and antimony may be chosen. With thallium, for example, the following results were obtained:—

Percentage of thallium in amalgam.	Molecular weight.	
	Found.	Calculated.
0·8191 p. c.	157·4	204·2
1·666 ,,	183·5	204·2
2·894 ,,	174·3	204·2
3·290 ,,	183·9	204·2

No appreciable change is produced on concentration. But with antimony, the molecular weight increases proportionately to the amount present, thus:—

Percentage of antimony in amalgam.	Molecular weight. Found.	Calculated.
1·117 p. c.	134·2	120·3
1·526 „	155·4	120·3 to 240·6
2·257 „	193·4	120·3 to 240·6
3·289 „	294·6	240·6 to 481·2 ?

Here an association of atoms is evidently in progress.

It may appear startling that the molecular weight of the metals sodium, potassium and barium are given as half their atomic weights. From the formula employed in calculation, it will be seen that this is on the assumption that the molecular formula of mercury is Hg_1. There are strong reasons in favour of this supposition, and the whole question will be discussed in the complete paper. But, at present, it may be taken as the most convenient way of stating results. The author would not wish to commit himself to any positive assertion on the point, except in so far as the accuracy of the experimental data are concerned. The numbers have been amply confirmed by repetition, and must be taken as accurate within from 1 to 5 per cent. of the quantity measured.

The author is now occupied in extending these results, and in confirming them by the depression of the melting point method.

27. "The application of Raoult's depression of melting point method to Alloys." By C. T. Heycock, M.A., and E. H. Neville, M.A.

The result of Raoult's investigations on the lowering of the freezing points of solutions "that one molecular proportion of any substance dissolved in 100 molecular proportions of any solvent whatever lowers the freezing point of that solvent 0·62° C." has not apparently been tested by the dissolution of metals in metals.

The authors therefore present the results of some preliminary experiments on the change in the solidifying point of tin caused by the addition of small quantities of other metals. From repeated experiments, they have confidence that the numbers obtained are approximately correct, though they reserve for a future paper details of the method of experiment and the conclusions which may be drawn from the results. For the present, it is sufficient to state that the dissolution of a metal in tin appears to follow the same laws as that of compounds in other solvents, *i.e.*, (1) That the fall in temperature of the solidifying point is directly proportional to the weight of metal added. (2) That the fall of temperature is inversely as the atomic (molecular?) weight of the metal added. The experiments were conducted by melting a mass of 400 grams of tin, and by means of

a mercury thermometer, using a reading telescope, the solidifying point was determined whilst the mass was kept rapidly stirred. Slight surfusion, usually three or four tenths of a degree, was generally noticed. The tin was then re-melted, and from 1 to 3 grams of metal added, and the solidifying point again determined. In some cases where the metals alloy with difficulty, portions of the 400 grams of tin were withdrawn, and, whilst fused under borax in a gas furnace, known weights of the other metals were added, and then this concentrated alloy was added to the bulk of the tin. Another gram or two of the metal was then added, and the experiments repeated. The average melting point of the tin used was 226·4° C. Working as above described, the authors find that one atomic proportion of each of the following elements dissolved in 100 atomic proportions of tin causes the following falls of temperature:—

Zn	2·53°
Cu	2·47
Ag	2·67
Cd	2·16
Pb	2·22
Hg	2·3
Al	1·34
Sb	2·0 (rise).

The facts that aluminium produces a fall only one-half that of the other elements, and antimony produces a rise, are they think of especial importance.

They hope shortly to communicate a more complete paper to the Society, and intend using other solvents such as Na, Cd, Pb, Hg, &c. They also propose to investigate the behaviour of those alloys which appear to be true compounds, and to find out to what extent of concentration the fall of temperature remains proportional to the weight of metal added, &c.

Discussion.

Dr. Armstrong said that notwithstanding the apparent regularity and simplicity of the results, he was not prepared to accept them as in the least degree final. There was not sufficient evidence in his opinion that the effect observed was not in part at least the outcome of a change in the molecular composition of the solvent; this objection had already been formulated by himself as well as by Professor J. J. Thomson and no one had as yet replied to their criticisms (*cf. Brit. Ass. Report*, 1888; *Report of Electrolysis Committee*). The question was one of fundamental importance in relation not only to the

determination of molecular weights of dissolved substances, but also to the interpretation of the phenomena of electrolysis and chemical change generally. The results obtained by Raoult's methods were, he thought, comparable with those obtained by determining the specific heats of the elements; in the latter case the observations were undoubtedly made with masses of molecules, which probably were of varying degrees of atomic complexity (*cf. Brit. Ass. Report*, 1885, p. 962), and yet the results were found to be such as to justify conclusions being drawn as to the relative magnitudes of their fundamental constituents—the atoms. In the same way it was possible that the results obtained by Raoult's method by means of observations on the behaviour of molecular complexes might afford the means of deducing the relative magnitudes of the fundamental molecules comprising the complexes, but not of the actual complexes operated with. The formation of compounds which undoubtedly took place in the case of sodium, for example, must influence the results.

Mr. Crompton asked Professor Ramsay whether he had examined solutions of strengths other than those given. He drew attention to Beckmann's recent experiments on the lowering of the freezing point; these show that the true molecular weight was only obtained when solutions were used the concentration of which was allowed to vary only within certain narrow limits; and that if the solutions were too dilute the molecular weight obtained from the lowering of the freezing point was too low, while if the solutions were too concentrated, it was too high. In some cases the variation of the number obtained with the concentration was enormous. The same would probably be the case for the reduction of the vapour-pressure. The results brought forward were undoubtedly of the greatest interest, but he thought that the method had not been so thoroughly investigated as to give them an absolute value as molecular weight determinations.

Mr. Pickering said that when the freezing points of mixtures of sulphuric acid and water were plotted out in a form which should, according to Raoult, give a straight line, they gave a most irregular figure. Between 0 and 100 per cent. the solidifying point sunk twice below $-40°$, and rose twice to $+10°$. The extreme end of the figure (for weak solutions) is, no doubt, irregular and curvilinear like the rest of it, and can be called straight only because the irregularity and curvature are lost in the comparative magnitude of the experimental error. It was not fair to consider evidence deduced from such a source in the same light as that deduced from gaseous densities, where any appreciable deviation from straightness is found only at the extreme ends of the figure, and where the deviation is of the same regular character in every case.

Mr. Groves suggested that although compounds of the metals and mercury could be formed, it was possible that these underwent dissociation when dissolved in mercury.

Professor Carey Foster remarked, that in the case of weak solutions the temperature at which ice forms is determined; but in the case of stronger solutions the temperature is often that at which a hydrate forms: this probably was the explanation of the peculiar curve described by Mr. Pickering. Much depended on the definition given of a molecule, whether it is defined as that smallest quantity capable of existence *per se*, or as that quantity which produces a given effect in depressing vapour-pressure, or freezing point, &c. The two magnitudes were not necessarily the same. The relation observed could hardly be accidental; yet he thought that the value obtained might be a quantity connected with the molecular weight, but not necessarily identical therewith.

Mr. Howard said the main question was, did compounds of mercury with the metals exist at the high temperatures at which the observations were made?

Professor Ramsay, in replying, argued that the existence of a compound of the metal with the solvent—in this case mercury—would give an increased molecular weight; and that, although such compounds existed in many cases at low temperatures, yet at the boiling point of mercury they appeared to be decomposed. The compound of copper and mercury, however, was an exception, inasmuch as it was not dissolved to any great extent by boiling mercury. Hence experiments with copper could not be carried out.

Substances in dilute solutions must be regarded as in the gaseous state, their molecules being so far distant from each other as not to exert appreciable attraction on each other; and as occupying but a small portion of the space they inhabit. It has long been argued that the molecular complexity of the gases hydrogen, oxygen and nitrogen must be the same, inasmuch as these elements have equal coefficients of expansion within the widest limits of temperature. A similar argument applies to substances in dilute solutions; it is much more probable that they have a simple and similar molecular structure than that the molecules, if complex, dissociate to an equal extent on equal rise of temperature or on equal alteration of concentration.

As regards the empirical nature of Raoult's laws, it is paralleled by the empirical nature of Boyle's and Gay-Lussac's laws, that is, such laws are merely approximations to truth and depend on the fact that the molecules are sensibly beyond the sphere of each other's attraction and themselves occupy no appreciable space. Hence their inapplicability at high concentrations. Just as gases deviate at high

pressures from the laws of elasticity, when definite compounds are formed, as instanced by Mr. Pickering in the case of mixtures of sulphuric acid and water, each such compound acts as a homogeneous substance—as a solvent of definite molecular weight, with a definite melting point, which is lowered by the addition of one or other constituent, as it would be by the addition of a substance different from either constituent, though probably not to a similar extent, owing to further reactions between the solvent and the added constituent, water or sulphuric acid, as the case might be.

28. "Some compounds of Tribenzylphosphine Oxide." By N. Collie, Ph.D., F.R.S.E.

Some time ago, the author, in conjunction with Prof. Letts, published an account (*Trans. Roy. Soc. Edin.*, **30**, Part I, 181) of the salts of tetrabenzylphosphonium. One of the compounds mentioned, the oxide of tribenzylphosphine, has been further examined. When treated with fuming nitric acid, tribenzylphosphine oxide yields a trinitro-derivative, $(C_7H_6{\cdot}NO_2)_3PO$, which is probably reduced by the action of tin and hydrogen chloride to a triamido-derivative. If the oxide be heated at 170° C. with sulphuric acid, a trisulphonic acid results, $(C_7H_6{\cdot}SO_3H)_3PO$. In both cases the introduced group takes up the para-position, as on oxidation *p*-nitrobenzoic and *p*-sulphobenzoic acids are obtained. On treatment with acetyl chloride the oxide yields a simple addition product, $(C_7H_7)_3PO{\cdot}C_2H_3OCl$. It also combines with hydrogen chloride and bromide, yielding compounds of a complicated structure agreeing with the corresponding triethylphosphine oxide-derivative, *e.g.*, $5(C_7H_7)_3PO{\cdot}4HCl$.

Tribenzylphosphine oxide therefore differs in several respects from the oxides of the tertiary phosphines of the fatty series. It does not form such stable compounds, neither is the oxide itself capable of resisting oxidising agents to the same extent. On the other hand, however, some of the derivatives, although complicated in their structure, seem to be analogous to the corresponding derivatives in the fatty series.

Discussion.

Professor Ramsay drew attention to the remarkable composition and stability of the molecular compounds obtained by Dr. Collie; he thought it was becoming essential to include and discuss such molecular compounds in a special chapter.

29. "Contributions to our knowledge of the Isothiocyanates." By Augustus E. Dixon, M.D.

The author describes a number of compounds obtained from various thiocarbimides by combination with basic substances.

The first two are members of the little known series of benzylated thiocarbamides. *Ethylbenzyl thiocarbamide*, EtNH·CS·NHBz, from ethyl thiocarbamide and benzylamine, crystallises in white needles melting at 102—103°. The corresponding *phenylbenzyl thiocarbamide*, PhNH·CS·NHBz, forms short, thick prisms; m. p. 153—154°.

The next three compounds are semithiocarbazides, and are obtained by the action of phenylhydrazine on the corresponding thiocarbimides. *Ethylphenyl semithiocarbazide*, EtNH·CS·NH·NHPh, forms glassy prisms melting at 121—122° without decomposition. A very delicate test for this substance consists in adding a few drops of ferric chloride to its solution in alcohol; a blood-red colour is produced, changing rapidly to dark green. It is remarkable that the m. p. of a metameric compound, PhNH·CS·NH·NHEt, obtained by Fischer (*Annalen*, **199**, 296), is much lower, viz., 109—110°. *Acetylphenylsemithiocarbazide*, AcNH·CS·NH·NHPh, forms thick, white prisms melting at 178—179°, while the analogous *benzoylphenylsemithiocarbazide*, PhCO·NH·CS·NH·NHPh, crystallises in silky, asbestos-like needles which do not melt at 220°.

The remaining compounds (together with the two last mentioned) were obtained during an investigation of thiocarbamides containing *acid* radicles, viz., *acetylorthotolylthiocarbamide*, AcNH·CS·NHTo, which crystallises in lemon-yellow prisms, m. p. 184°; and *benzoylphenylethylthiocarbamide*, PhCO·NH·CS·NEtPh, which crystallises in yellow prisms melting at 133—134°.

30. "The constitution of Primuline and allied sulphur-compounds." By Arthur G. Green.

The product obtained on heating 2 mol. props. of paratoluidine with 2 atomic props. of sulphur until the evolution of hydric sulphide has ceased, chiefly consists of a mixture of Merz and Weith's thiotoluidine (diamidoditolyl sulphide, $(C_7H_6{\cdot}NH_2)_2S$), and a base, $C_{14}H_{12}N_2S$, containing 4 atoms of hydrogen less, which, as proposed by Jacobson, may be called "dehydrothiotoluidine." If the amount of sulphur be doubled, thiotoluidine is almost absent, the product containing, together with dehydrothiotoluidine, a more highly condensed base which probably has the formula $C_{28}H_{18}N_4S_3$. The monosulphonic acid of the latter base possesses the peculiar property of readily dyeing unmordanted cotton in an alkaline bath a pure primrose-yellow, and whilst on the fibre may be converted into a diazo-compound which may there and then be caused to interact with amines and phenols. This product, discovered by the author in February, 1887, was put on the market under the name of "Primuline," and is

largely employed for cotton-dyeing on account of the great range of fast shades that may be obtained with it.

Dehydrothiotoluidine, $C_{14}H_{12}N_2S$, is isolated from the melt by boiling with somewhat diluted chlorhydric acid, precipitating with soda, distilling and crystallising from amyl alcohol. It forms long, yellowish, iridescent needles melting at 191° (uncorr.), and boils at 434° (uncorr., bar. 766 mm.). It is moderately soluble in hot amyl alcohol, readily in acetic acid. Its alcoholic solution exhibits a violet-blue fluorescence, which also characterises all its derivatives. By diazotisation and by the constitution of the acetyl-derivative, it is shown that one of the nitrogen atoms is in the form of NH_2, whilst the other is nitrilic. By boiling with zinc-dust and HCl it is reduced to a base of quite different properties. On distillation with zinc-dust it yields paratoluidine. From these and other facts the author deduces the formula $CH_3{\cdot}C_6H_3{<}^{N:CH}_{\ \ S\ \ }{>}C_6H_3{\cdot}NH_2$, which represents dehydrothiotoluidine as derived from thiotoluidine by removal from a CH_3 and an NH_2-group of four atoms of hydrogen.

The *acetyl-derivative*, $C_{14}H_{10}SN(NH{\cdot}CO{\cdot}CH_3)$, forms white prisms which melt at 227° (uncorr.). It combines with bromine. The *dimethyl-derivative*, $C_{14}H_{10}SN{\cdot}N(CH_3)_2$, crystallises in yellowish plates melting at 195—196°. The *trimethylammonium* salts are easily soluble in water and have strong tinctorial power, dyeing silk a pure greenish-yellow with a green fluorescence. The *monosulphonic acid*, $C_{14}H_9SN(NH_2)(SO_3H)$, crystallises from water either in flattened, yellow needles ($+H_2O$), or in orange, aggregated leaflets ($+2H_2O$). The salts of the sulphonic acid are mostly colourless, and have no affinity for cotton. The ammonium and copper salts are very characteristic: the latter is an insoluble reddish-brown precipitate; the former crystallises in sparingly soluble, white, crystalline plates.

Primuline-base.—As this compound is also obtained by heating thiotoluidine or dehydrothiotoluidine with sulphur, it would appear that its formation is preceded by that of these compounds. The difficulty of isolating it in the pure state has hitherto prevented the determination of its composition with certainty, but it appears to have the formula $C_{28}H_{18}N_4S$, and hence probably has the constitution $CH_3{\cdot}C_6H_3{<}^{N:CH}_{\ \ S\ \ }{>}C_6H_2{<}^{N:CH}_{\ \ S\ \ }{>}C_6H_2{<}^{N:CH}_{\ \ S\ \ }{>}C_6H_3{\cdot}NH_2$.

Primuline-base is a bright yellow powder, which is nearly insoluble in all solvents. Its salts are dark-coloured and are decomposed by water, in which they are insoluble. It is an extremely stable compound, and may be heated above 400° C. without decomposing.

Discussion.

Mr. Wynne took exception to the formulæ proposed by Mr. Green, regarding it as improbable that dehydrothiotoluidine contained a closed chain of eight atoms, and that the sulphur-atom should be connected in the ortho-position in the one and the meta-position in the other nucleus.

31. "The determination of the constitution of the heteronucleal $\alpha\beta$- and $\beta\beta$-di-derivatives of Naphthalene." (Second Notice.) By Henry E. Armstrong and W. P. Wynne.

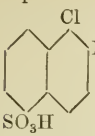
This communication is a continuation of that brought under the notice of the Society at the previous meeting (*cf. Chem. Soc. Proc.*, 1889, No. 64, pp. 34—37), and is an account of the constitution of the three isomeric sulphonic acids prepared from 1 : 2 α-chloro-β-naphthylamine in the manner described in the former notice.

In displacing the NH_2 radicle of the amidochlorosulphonic acids by v. Baeyer's hydrazine method (*cf.* Haller, *Ber.*, 1885, 90), the authors were for some time seriously misled, as the products obtained were impure, owing to the extreme sensitiveness of the hydrazines to the action of hydrogen chloride in presence of cuprous salt; they behave, in fact, as diazo-compounds, and it is therefore essential not only to avoid the use of cupric chloride and to employ cupric sulphate, but also to purify the hydrazines.

Constitution of the No. 1 *Acid.*—As already mentioned, this acid yields the Dahl modification of betanaphthylaminesulphonic acid on reduction. This statement is based both on the study of the properties of the reduction product, and on the further observations that it is converted by Sandmeyer's method into a chloronaphthalenesulphonic acid, yielding a monohydrated sodium salt crystallising in scales, and a chloride which crystallises from a mixture of petroleum spirit and benzene in well-defined prisms melting at 70°; and that this sulphochloride yields on distillation with PCl_5 a dichloronaphthalene which crystallises from alcohol in long slender needles melting at 48° (*cf. Brit. Ass. Report*, 1888; *Chem. News*, **58**, 295).

The chlorosulphonic acid obtained from the No. 1 chloramidosulphonic acid yields a monohydrated potassium salt crystallising in small elongated plates; a chloride which crystallises from benzene in small, well-defined prisms melting at 95°; an amide crystallising from dilute alcohol in slender needles melting at 225°; and a dichloronaphthalene crystallising from alcohol in scales melting at 107°.

It was pointed out in the previous communication (*cf.* these Proceedings, 1889, p. 35) that γ-dichloronaphthalene must be regarded as the axially symmetric 1 : 4′ $\alpha\alpha$-heteronucleal dichloronaphthalene;

the formula representing the constitution of the No. 1 acid will therefore be 

, as this results on superposing the formula of the 1 : 4′ chloronaphthalenesulphonic acid derived from it and that of the parent 1 : 2 chlorobetanaphtbylamine. Displacing chlorine by hydrogen, the formula of the Dahl acid results, viz.,

; whence it follows *that η-dichlororonaphthalene, m.p.* 48°, *is the* 1 : 3′ *dichloronaphthalene.* This result is in harmony with that arrived at by Erdmann and Kirchhoff, and serves to justify the interpretation which they have given of their synthesis of η-dichloronaphthalene.

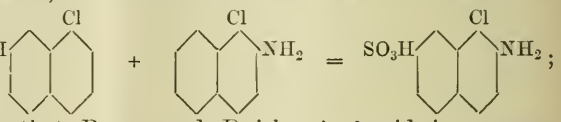
The No. 1 acid is converted by Sandmeyer's method into a dichloronaphthalenesulphonic acid which yields a potassium salt crystallising in scales; a chloride crystallising from benzene in massive prisms melting at 104°; an amide crystallising from dilute alcohol in slender elongated plates melting at 218°; and a trichloronaphthalene crystallising from alcohol in long slender needles melting at 78—78·5°. Dichloronaphthalene melting at 34°, which is obtained by displacing NH_2 in α-chlorobetanaphthylamine by Cl, on sulphonation yields at least two acids (*Brit. Ass. Report*, 1888; *Chem. News*, **58**, 295), from each of which the dichloronaphthalene can again be obtained by hydrolysis; one of these acids—the chief product—is undoubtedly identical with that prepared from the No. 1 chloramido-acid, as its chloride crystallises in massive prisms melting at 105°, its amide in needles or slender scales melting at 216·5—217°, and the trichloronaphthalene prepared from it in needles melting at 78°.

Constitution of the No. 3 *Acid.*—On reduction this acid yields Bayer and Duisberg's betanaphthylamine-δ-sulphonic acid; the reduction-product was converted by Sandmeyer's method into a chloronaphthalenesulphonic acid from which a chloride was prepared crystallising from benzene in prisms melting at 86°, and an amide crystallising from dilute alcohol in minute prisms melting at 175°; on distilling the sulphochloride with PCl_5, δ-dichloronaphthalene, m. p. 114°, was obtained (*cf. Brit. Ass. Report*, 1888).

The chlorosulphonic acid prepared from the No. 3 acid yields a monohydrated potassium salt crystallising in small, thin scales; a chloride crystallising from a mixture of benzene and petroleum spirit in well-defined, elongated prisms melting at 93—94°; and an amide crystallising from dilute alcohol in long, slender needles

melting at 185—186°; the dichloronaphthalene, prepared from the sulphochloride, crystallised from alcohol in aggregates of short, slender needles melting at 63·5—64°: it was characterised by the authors' method, by sulphonation—the chloride of the resulting sulphonic acid crystallised in needles which became opaque after some time, and melted at 117—118°. This dichloronaphthalene is obtained, as the authors have shown, from Arnell's β-chloronaphthalenesulphonic acid (*Brit. Ass. Report*, 1888; *Chem. News*, 58, 295); from the Badische betanaphthylaminesulphonic acid (*ibid.*; these Proceedings, 1888, No. 58, p. 105); from parachlorophenylparaconic acid (Erdmann and Kirchhoff; *cf.* these Proceedings, 1889, No. 61, p. 7); and from Cleve's *0*-α-nitronaphthalene-β-sulphonic acid (these Proceedings, 1889, No. 62, p. 18). As it is a heteronucleal α-β-derivative, it must by exclusion be the 1 : 2′-compound, as the only alternative 1 : 3′ formula has been proved above to belong to η-dichloronaphthalene, m. p. 48°.

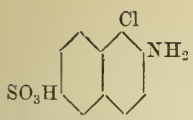
Superposing the formula which expresses the constitution of the new chlorosulphonic acid from the No. 3 acid and that of the parent chloramidonaphthalene, the formula of the No. 3 acid is shown to be as follows:—



whence it follows that Bayer and Duisberg's δ-acid is as more frequently supposed a 2 : 2′-derivative.

The dichloronaphthalenesulphonic acid prepared by Sandmeyer's method from the No. 3 acid yields a monohydrated sodium salt crystallising in elongated, rectangular plates; a chloride crystallising from benzene in small, well-defined prisms melting at 122—123°; and an amide crystallising from dilute alcohol in long, slender needles melting at 225—226°; the corresponding trichloronaphthalene crystallises from alcohol in hemispherical aggregates consisting of microscopic needles melting at 83—84°.

Constitution of the No. 2 Acid.—The chloronaphthalenesulphonic acid prepared from the No. 2 chloramidosulphonic acid yields an anhydrous potassium salt crystallising in small granules; a chloride crystallising from benzene in aggregates of minute diamond-shaped plates which afterwards grew into the form of opaque hemispherical aggregates melting at 112—113°; an amide crystallising from dilute alcohol in small scales melting at 185—186°; and a dichloronaphthalene melting at 48—49°: this acid is consequently identical with that described by Cleve (*Berichte*, 1887, 74), and corresponds with η-dichloronaphthalene in constitution. From this it follows that the constitution of the No. 2 acid is expressed by the formula



; and also that it is derived from the Brönner betanaphthylaminesulphonic acid: that this is the case the authors have been able to place beyond doubt, although owing to its peculiar behaviour on reduction they have not succeeded in converting it directly into the Brönner acid.

The sodium salt of the No. 2 acid is so sparingly soluble in cold water that the reduction has to be effected at a temperature of 50—60°, and then proceeds very slowly: the liquid becomes of a dark brown colour, and yields a very dark-coloured sodium salt on evaporation; this salt is soluble in 90 per cent. alcohol. On acidulating a solution of the sodium salt, only a relatively very small amount of precipitate was obtained; the acid thus prepared, although evidently very impure, gave on treatment by Sandmeyer's method a chlorosulphonic acid from which a chloride crystallising in small prisms melting at 107° and an amide crystallising in needles melting at 183° were obtained. The chloride and amide of the chlor-acid prepared by Forsling (*Berichte*, 1887, 80) from the Brönner acid have similar properties to those observed by the authors in the case of their product, and there can be little doubt therefore that the Brönner acid is formed. The chief product of reduction, however, is a very soluble acid—perhaps, a hydro-derivative. If placed in contact with sodium amalgam under conditions similar to those observed in reducing the No. 2 acid, the sodium salt of the Brönner acid appears to slowly change, the solution becoming dark-coloured.

When the chlorobetanaphthol corresponding to chlorobetanaphthylamine is sulphonated, it yields a sulphonic acid which is undoubtedly a derivative of Schaeffer's betanaphtholsulphonic acid—an acid which itself is convertible into and may be obtained from Brönner's betanaphthylaminesulphonic acid—inasmuch as it yields the same bromhydroxyquinonesulphonate as the Schaeffer acid on treatment with bromine, and may be converted into the Schaeffer acid by reduction with sodium amalgam. An attempt to prepare this naphthol-derivative from the No. 2 acid was unsuccessful, owing to the extreme stability of the diazo-derivative of the latter acid; on the other hand, on heating the chloronaphtholsulphonate with ammonia under pressure, a complex action took place, but a small quantity of an acid was ultimately obtained which, judging from the characteristic appearance of its sodium salt, was the No. 2 acid.

The dichloronaphthalenesulphonic acid prepared by Sandmeyer's method from the No. 2 acid gave a sodium salt crystallising in minute scales; a chloride crystallising from benzene in small aggregates of

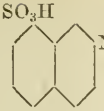
minute prisms melting at 165—166°; an amide crystallising from dilute alcohol in slender, yellow needles melting at 187—188°; and a trichloronaphthalene crystallising from alcohol in tufts of short, slender needles melting at 92°. A trichloronaphthalene of the same melting point was obtained by submitting the chlorobetanaphthol-sulphonate above-mentioned to the action of PCl_5.

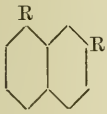
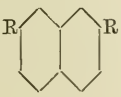
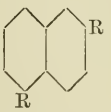
The results obtained in the case of the No. 2 and No. 3 acids prove that betanaphthylamine-δ-sulphonic acid and corresponding di-derivatives of naphthalene (*e.g.*, δ-dichloronaphthalene, m. p. 114°) are 2 : 2′ compounds; and that the isomeric Brönner acid and corresponding di-derivatives (*e.g.*, ϵ-dichloronaphthalene, m. p. 135°) are 2 : 3′ compounds. They conclusively refute Erdmann's statement (*Berichte*, 1888, 639): "Diese Frage (as to whether the Brönner and δ acids are respectively 2 : 3′ and 2 : 2′ compounds, or *vice versâ*) ist nur durch synthetischen Aufbau dieser oder ähnlichen Verbindungen zu lösen"—indeed, notwithstanding it has been their privilege to confirm Erdmann and Kirchhoff's conclusions, the authors remain of the opinion that a synthetic method, such as these chemists have so successfully employed, does not and cannot afford a final solution of the problem, although their results undoubtedly serve to increase our belief in the general trustworthiness in such cases of conclusions based on the application of synthetic methods.

The results also establish the correctness of the opinion, long held and frequently expressed by the authors, based on the higher melting points of the uniform ϵ-di-derivatives in comparison with the isomeric δ-di-derivatives, that the ϵ-derivatives are symmetrically constituted; this conclusion, in fact, is probably the most important outcome of the experiments, as it affords conclusive proof of the influence of symmetry as the determining cause in the case of naphthalene-derivatives of high melting point and slight solubility, &c.

It has already been pointed out that the dichloronaphthalene-sulphonic acid prepared from the No. 1 acid is identical with the chief product of sulphonation of 1 : 2 dichloronaphthalene; the dichloro-acid prepared from the No. 2 acid is found in like manner to be identical with the second acid formed on sulphonating the dichloronaphthalene in question. As the one acid is an alpha-sulphonic acid and the second a beta-sulphonic acid formed by displacement of the hydrogen-atom contiguous to that which is displaced in the α-sulphonic acid, the authors are of opinion that the betasulphonic acid is a product of isomeric change and not a product of initial action; they propose to investigate this question in the manner already adopted with success in the case of the acids derived from β-chloro-, β-bromo- and β-iodo-naphthalene.

Lastly, it may be pointed out that as the Badische betanaphthyl-

aminesulphonic acid is now proved to have the constitution represented by the formula  , the remarkable fact that this acid alone of the four known heteronucleal betanaphthylaminesulphonic acids does not afford azo-colours must be regarded as a result of a "protecting influence" of the amido and sulphonic radicles on the included α-hydrogen atom, and the non-occurrence of the isomeric change which would be involved in the conversion of the diazoamido-compound initially produced by the action of the diazo-compound into the quinonoid azo-colour (*cf.* these Proceedings, 1888, No. 49, p. 29); it is noteworthy that the isomeric change does take place in the case of the corresponding hydroxy-acid (Bayer's croceinic acid) although the colour is formed but slowly, and it is not improbable that it may be found possible by varying the diazo-compound to obtain colours even from the Badische amido-acid. The authors propose to undertake experiments in this direction.

 2 : 1′	 2 : 2′	2 : 3′	 2 : 4′
Cl_2. M. p. 63·5°	Cl_2. M. p. 114°	Cl_2. M. p. 135°	Cl_2. M. p. 48°
$NH_2\beta\cdot SO_3H$ (Badische)	$NH_2\beta\cdot SO_3H$ (Bayer & Duisberg)	$NH_2\beta\cdot SO_3H$ (Brönner)	$NH_2\beta\cdot SO_3H$ (Dahl)
$OH\beta\cdot SO_3H$ (Bayer)	$OH\beta\cdot SO_3H$ (Casella)	$OH\beta\cdot SO_3H$ (Schaeffer)	$OH\beta\cdot SO_3H$ (Dahl)
$NO_2\alpha\cdot SO_2Cl$ M. p. 169°	—	—	$NO_2\alpha\cdot SO_2Cl$ M. p. 125°
—	$(SO_3H)_2$ (Ebert & Merz α)	$(SO_3H)_2$ (Ebert & Merz β)	$(SO_3H)_2$ (Armstrong & Wynne)
$Cl\alpha\cdot SO_2Cl$ M. p. 94°	—	—	$Cl\alpha\cdot SO_2Cl$ M. p. 114°
$Cl\beta\cdot SO_2Cl$ M. p. 129°.	$Cl\beta\cdot SO_2Cl$ M. p. 86°	$Cl\beta\cdot SO_2Cl$ M. p. 109°	$Cl\beta\cdot SO_2Cl$ M. p. 70°.

The constitution of a number of heteronuclear di-derivatives of naphthalene which are of importance as reference compounds is indicated in the foregoing table, the compounds being represented by the symbols of the constituent radicles. The authors take this opportunity of directing the attention especially of Continental colleagues to the desirability of adopting a uniform system of notation; they would advocate that which has long been in use by the Chemical Society, which consists in numbering the positions in the one nucleus 1, 2, 3, 4, and the corresponding positions in the second nucleus 1′, 2′, 3′, 4′. This method they regard as more rational, in view of the fact that naphthalene contains two like nuclei, than the practice now sometimes adopted of numbering the positions 1 to 8.

32. "Contributions to the knowledge of Citric and Aconitic Acids." By S. Skinner, B.A., and S. Ruhemann, Ph.D., M.A.

The authors have studied the action of phosphorus pentachloride on citric acid, following Pebal's directions (*Annalen*, 98, 67). They show that the product is a chloromonochloride formed by the displacement of the alcoholic hydroxyl and one of the carboxylic hydroxyls, it being uncertain, however, which of the three latter in citric acid is affected. The chloride is reconverted into citric acid by the action of water; when heated at 125°, it loses hydrogen chloride, yielding a product which water converts into aconitic acid; aniline transforms it into aconitylanilanilide, and it is similarly affected by treatment with orthotoluidine. The anilanilide yields the anilcarboxylic acid and aniline on hydrolysis, and the toluidine-derivative affords the corresponding toluidcarboxylic acid.

March 28th, 1889. Annual General Meeting. Mr. W. Crookes, F.R.S., President, in the Chair.

The President delivered an address, of which the following is an abstract:—

The number of Fellows of the Society is 1650, of whom 36 are honorary foreign members; at the same period last year there 1571 Fellows of whom 37 were honorary foreign members.

140 Fellows have been elected during the year.

23 Fellows have died during the year:—Professor Brazier, R. Cartmell, John Collins, J. J. Coleman, Professor H. Debray (Foreign Member), W. F. Donkin, H. C. Foote, Peter Griess, A. N. Gow, John Horsley, J. M. Kavanagh, J. D. Perrins, Dr. David Price, F. G. Ree, J. Robinson, W. O. Senior, J. Storey, James Taylor, J. S. Topham, Thomas Ward, Dr. W. Wallace, G. J. Wishart, John Williams.

16 Fellows have withdrawn:—R. Byramjee, C. B. Caswell, Dr. E. A. Cook, R. Coulthard, P. N. Datta, Charles E. Ellis, F. A. Genth, Jun., C. H. Gimingham, Andrew Henderson, Edward Hunter, W. J. Noble, Walter Pearce, Dr. B. W. Richardson, J. P. Smith, Ed. S. Spalding, and Oswald Wilkinson.

21 Fellows have been removed on account of arrears:—J. B. Bardsley, William Bedford, R. G. Blaine, Professor A. C. Dixon, A. E. Drinkwater, U. K. Dutt, Rev. W. H. Eley, E. H. Farmer, W. F. Fremersdorff, F. G. Holmes, J. J. Knight, J. L. Muspratt, Robert Marr, S. R. Pontifex, Thomas Perry, R. H. Ridout, G. H. Rutter, Wm. Robinson, Franz Rindskopf, F. M. Sexton, and J. W. Stevens.

In the year 1888 there were 75 original papers published in the Transactions, occupying 895 pages, compared with 88 papers of 871 pages in 1887. The Abstracts in 1888 occupy 1351 pages, compared with 1159 in 1887. The number of Abstracts is 2470 compared with 2277 in 1887.

103 papers have been communicated to the Society this session.

The Library continues to increase, and every year is becoming richer in rare volumes and books of reference. The duplicate library for lending is also becoming increasingly useful. The following table shows the present state of the shelves:—

	March 31st, 1888.	Addition in 1888-89.	Present State.
Volumes of systematic works.....	2,780	142	2,922
Volumes of journals.....	5,119	355*	5,474
Volumes of duplicate journals for circulation.	941	143†	1,084
Pamphlets.....	1,410	16	1,426
	10,250	656	10,906

* Including 170 vols. *Dingler's Polytechnisches Journal.*
† Including 93 vols. *Dingler's Polytechnisches Journal.*

The expenditure under this head for the current year is £308 5*s.* 6*d.*

Referring to his remarks of last year relating to the publication of the same paper in several journals, the President pointed out that the Council have resolved that no memoir is to be published which has previously appeared in any foreign journal unless it is specially recommended by the Publication Committee and approved by the Council. The reasons for this resolution are not hard to seek, the chief being that the reputation of the Society, as the original channel of the researches in question, is imperilled or at least obscured.

After speaking with approval of the recent protest against examinations, the President drew attention to an evil threatening, if not in actual operation, against which, he thought, timely protest should be raised, viz.. the system of "sealed papers." Everyone knows that on the Continent, and more especially in France, it is common for some one who has come, as he thinks, near the solution of some important question, to write out a sketch of his incomplete results, seal it up, and deposit it for safe keeping with the President or the Secretaries of some learned Society. Here it may lie, perhaps for years, until the author requests that it may be opened and read before the Society. The original plea for this practice was that the author's priority should be guaranteed against others who might possibly lay claim to his ideas. But priority can be quite as effectually secured by a brief preliminary notice read before some Society or sent to some journal, in which the author reserves to himself the further investigation of the subject. Such reservations are invariably respected among men of honour.

Reference was made to Krüss's instructive discovery that nickel and cobalt contain a common hitherto unsuspected constituent; and to the recently published posthumous memoir, in which Wroblewski's observations on the compressibility of hydrogen at temperatures ranging from that at which water boils to that at which oxygen boils

(−182·4°); as Wroblewski comes to the conclusion that the critical temperature of hydrogen is −240°, and its critical pressure 13·3 atmospheres, it is improbable that either Pictet or Cailletet ever succeeded in liquefying hydrogen.

It was announced that the Council had resolved that in future the balloting for Fellows at the Meetings should be conducted by means of papers.

The President then proceeded to give an account of the history of the so-called rare earths, as they have been brought to light and distinguished by the aid of the spectroscope, particularly with reference to his own researches. In the following table is given a list of the so-

	Atomic weight of metal and formula of oxide.	Gives spectrum by—	Component meta-elements according to— Crookes (1886).	Nilson and Krüss (1887).
Didymium	Neodymium— 140·3, Nd_2O_3. Praseodymium— 143·6, Pr_2O_3. Unnamed.	Absorption.	$D\alpha$ $\lambda = 475$	$Di\alpha$ $Di\beta$ $Di\gamma$ $Di\delta$ $Di\varepsilon$ $Di\eta$ $Di\theta$ $Di\iota$ $Di\varkappa$
Decipium				
Samarium	150·12, Sm_2O_3.	Absorption and phosphorescence.	$S\delta$ $G\varepsilon$ $G\gamma$ $G\theta$	$Sm\alpha$ $Sm\beta$
Lanthanum	138, La_2O_3.	Phosphorescence.		
Erbium	166, Er_2O_3.	Absorption and phosphorescence.	λ 550 λ 493	$Er\alpha$ $Er\beta$
Philippium	45—48, PpO.	Phosphorescence.		
Holmium	—	Absorption.	—	$X\alpha$ $X\beta$ $X\gamma$ $X\delta$
Thulium	170·7, Tm_2O_3.	Absorption.		$Tm\alpha$ $Tm\beta$
Dysprosium	—	Absorption.	λ 457—448	$X\zeta$ $X\varepsilon$ $X\eta$
				Lecoq de Boisbaudran.
Yttrium	88·9, Yt_2O_3.	Phosphorescence.	$G\alpha$ $G\beta$ $G\delta$ $G\zeta$ $G\eta$	$Z\alpha$ Tb Yt
Terbium	124·7, Tb_2O_3.			
Gadolinium ($Y\alpha$)	—	Phosphorescence.	$G\beta$ $G\zeta$	
Ytterbium	173·01, Yb_2O_3.	Phosphorescence.		
Scandium	44·03, Sc_2O_3.			

called "rare elements," with which he has been specially occupied during the last seven or eight years. Column 1 gives the names by which they are commonly known. Column 2 gives their atomic weights, &c. Column 3 shows in what manner they come under the domain of spectroscopy; and columns 4 and 5 give the components or meta-elements into which some of these bodies have been decomposed in 1886 by the President, and in 1887 by Krüss and Nilson. A judicial leniency has been exercised in retaining candidates in the first column. Thus, it may be doubted whether decipium, philippium, or gadolinium should have been retained. But when doubts have been cast on the integrity of nearly all the occupants of this column the line cannot be drawn too strictly.

The Didymium Group.—Didymium from samarskite was found by Delafontaine in 1878 to differ somewhat from ordinary didymium extracted from cerite and gadolinite, and he separated from it what he regarded as a new element—decipium; nine months later Lecoq de Boisbaudran announced the discovery of samarium in samarskite, pointing out that its absorption-spectrum was that of decipium, together with two additional bands. In 1885 Carl Auer showed that it was possible to cleave didymium in a certain direction into neodymium and praseodymium. If the spectra of these latter be subtracted from the spectrum of the substance previously regarded as didymium, two bands remain; so that, assuming the argument from absorption-spectra to be a legitimate one, it is to be assumed, said the President, that didymium contains yet a third substance: but, he added, didymium had undergone other cleavages in his laboratory; he had not yet decided, however, whether we shall have to recognise further decomposition of neodymium and praseodymium, or whether the original didymium is capable of being resolved differently, according to the manner in which it is treated: working on the spectra of didymium from various sources, the conclusion was more and more forced on him that didymium must not be regarded as compounded of two elements only, but rather as an aggregation of many closely allied bodies. Later researches of Krüss and Nilson have led them to the same conclusion. They have discovered that in didymium obtained from some minerals one of the fainter lines of the normal didymium spectrum is strong, while others usually stronger are almost or quite absent. In this way, by examining a great number of minerals, they found anomalies occurred in the case of almost each of the old didymium lines, and therefore decided that it is a compound body, capable of resolution into at least nine separate components. Identical arguments are brought forward to prove that each of the other so-called elements, samarium, erbium, holmium, thulium, dysprosium, &c., are compounds of many closely allied

bodies. Krüss and Nilson question the possibility of resolving the erbia and didymia earths into their several ultimate constituents by a fractionated decomposition of the nitrates. In fact they assert that by means of the methods of separation at present known it would be almost impossible to completely isolate any single constituent of the mixed earths. They therefore propose, as he had previously done, a method by which we may certainly arrive nearer to the mark and dispense with much tedious fractionation. If we examine the minerals which contain these rare earths we find they occur in very different states of mixture or combination. Sometimes many of the constituents which we wish to separate are conjointly present, and sometimes but few. The desired differentiation, in fact, has already been commenced by Nature. Krüss and Nilson, therefore, whichever ingredient they wish to separate, propose to operate on a mineral which contains that ingredient as far as possible in a state of isolation. In other words, they will take advantage of the work that Nature has already begun, and endeavour by refined chemical means to put the last finishing touches to her work.

The crude earth contained in any single mineral was examined as a whole, by Krüss and Nilson, without any attempt to separate the earths, although the composition of some of these minerals is extraordinarily complex.

In his own case the didymium earths, the examination of which led him to form the "one band one element" theory, said the President, were in a much more simple state, as the whole of the yttrium group, including erbium, holmium, thulium, &c., and others, had been removed, and the earth under examination probably contained little besides didymium and lanthanum, with traces only of samarium, yttrium, and calcium. But not even here was the earth under examination in a state of even approximate purity.

There are at least two points in these researches which illustrate the necessity of great caution in drawing conclusions from an examination of absorption-spectra. Kiesewetter and Krüss have examined gadolinite, and find that some constituents of didymium and samarium are absent, notably those which produce the group of lines in the green to which the President had referred; he, however, had worked in his own laboratory for the last two years almost exclusively on the earths from gadolinite—of which he had obtained a large quantity from Fahlun—and there is not the shadow of a doubt that in his gadolinite earths the lines reported absent by Kiesewetter and Krüss are present in abundance. Some hitherto unexplained condition doubtless rendered these lines invisible to Kiesewetter and Krüss; perhaps the presence of some other earths, or some condition of concentration or acidity. In the light of this knowledge he did not see how we can take Krüss and Nilson's or his own results as final.

Little is yet known concerning the influence of one body on another, but that little is of sufficient importance to make us very careful how we interpret absorption-spectra when uncorroborated by chemical results. Lecoq de Boisbaudran and Smith have pointed out some important modifications produced in absorption-spectra by an excess of acid, and later on Soret verified these observations. Again Brauner and others have recorded experiments on mixing solutions of didymium and samarium; they find, in the case of a didymium solution showing the group of three bands, $1/\lambda^2$ 430·4, 441·3, 454·6, that by adding a dilute solution of samarium, all three of these bands vanish without any appearance of any of the samarium bands, until a certain proportion is reached, when the samarium bands gradually come in their place. In his own experiments, he found that from a solution of erbia which originally shows no trace of the strong didymium band $1/\lambda^2$ 292, appreciable quantities of didymium can certainly be squeezed out by fractionation.

The Erbium Group.—The oxide ten years ago called erbia, and regarded as belonging to a simple elementary body, has been resolved by the investigations of Delafontaine, Marignac, Soret, Nilson, Cleve, Brauner, and others into at least six distinct earths—three of them, scandia, ytterbia, and terbia, giving no absorption-spectra, whilst others, erbia (new), holmia, and thulia, give absorption-spectra. According to Lecoq de Boisbaudran, holmium is a mixture of true holmium with dysprosium, but this latter, the President believes, consists of at least two simpler bodies; and fractionation experiments had led him to recognise the existence of still another earth of the erbium group.

The Yttrium Group.—Yttrium—the old yttrium—proves now to be not a simple element, but a highly complex substance. He had come to the conclusion, said the President, that it may be split up certainly into five and probably into six constituents. These constituents of the old yttria are not *impurities* in yttria any more than praseodymium and neodymium are impurities in didymium. They proceed from a real splitting up of the yttrium molecule into its components, and when this process is completed the old "yttria" has disappeared. One of the most distinct characteristics of "old yttria" is its very definite spark spectrum. To which of its components this spark spectrum belongs, he was not yet able to say. It is possible that the particular component to which the spark spectrum is due yields no phosphorescent spectrum. It is also possible that the spark spectrum, like "old yttria," may prove to be compound, and then the well-known lines it contains will have to be shared between two or more of the newly-discovered bodies. At present no single component of old yttria can lawfully lay claim to what may be called the paternal name; so in the present state of the question no one is

entitled to call one of the new bodies "yttria," and to characterise the remainder as impurities.

A possible explanation of the existence and nature of the new bodies into which "old yttrium" has been split up, and of parallel cases which will doubtless be found on closer examination, is this. Our notions of a chemical element must be enlarged; hitherto the elemental molecule has been regarded as an aggregate of two or more atoms, and no account has been taken of the manner in which these atoms have been agglomerated. The structure of a chemical element is certainly more complicated than has hitherto been supposed. We may reasonably suspect that between the molecules we are accustomed to deal with in chemical reactions, and the component or ultimate atoms, there intervene sub-molecules, sub-aggregates of atoms, or meta-elements, differing from each other according to the position they occupy in the very complex structure known as "old yttrium." The arguments in favour of the different theories are as yet not unequally balanced. But the assumption of compound molecules will perhaps account for the facts, and thus legitimate itself as a good working hypothesis, whilst it does not seem so bold an alternative as the assumption of eight or nine new elements.

A compound molecule may easily act as an element; of this, didymium is an example, having been subjected to the closest scrutiny by some of the ablest chemists in the world without being resolved.

We have, in fact, a certain number of reagents, operations, processes, &c., in use. If a body resist all these and behave otherwise as a simple substance, we are apt to take it at its own valuation and to call it an element. But for all that, it may, as we see, be compound, and as soon as a new and appropriate method of attack is devised we find it can be split up with comparative ease. Still, we must never forget that, however complex, it can hardly be resolved into more than two parts at one operation.

We need some criterion for an element which shall appeal to our reason more clearly than the old untrustworthy characteristic of having not as yet been decomposed. It may be that whatever body gives only one absorption-band is an element, but we cannot conversely say that an element may be known by its giving only one absorption-band, since most of our elements give no bands at all! Until these important and difficult questions can be decided, he had preferred to open what may be figuratively called a suspense account, wherein we may provisionally enter all these doubtful bodies as "meta-elements." But these meta-elements may have more than a mere provisional value. Besides compounds, we have hitherto recognised merely ultimate atoms, or the aggregations of such atoms into simple molecules. But it becomes more and more probable that between the

atom and the compound we have a gradation of molecules of different ranks, which, as we have seen, may pass for simple elementary bodies. It might be the easier plan, so soon as a constituent of these earths can be found to be chemically and spectroscopically distinguishable from its next of kin, to give it a name, and to claim for it elemental rank; but it seemed to him the duty of a man of science to treat every subject, not in the manner which may earn for him the greatest temporary κῦδος, but in that which will be of most service to Science.

Throughout the address, attention was directed to the various spectra, and to the methods of producing them; the action of different earths, &c., on phosphorescence spectra was also specially considered.

Professor Dewar proposed a vote of thanks to the President, coupled with the request that he allow his address to be printed; Dr. Gladstone seconded the motion, which was carried by acclamation. The President briefly responded.

Dr. Russell, the Treasurer, then gave an account of the financial position of the Society. The receipts by admission fees and subscriptions had been £3,402; by sale of Journal, £365 3*s.* 3*d.*; and by dividends on invested capital, £344 4*s.* 3*d.* The expenses on account of the Journal had been £2,350 5*s.* 11*d.*; on account of the Abstracts of Proceedings, £164 4*s.* 7*d.*; on account of the Library, £308 5*s.* 6*d.*; the total expenditure being £3,429 18*s.* 3*d.* £500 had been invested in Metropolitan Board of Works 3½ per cent. stock, and the balance in hand was £1,833 10*s.* 6*d.*, the balance at the corresponding period last year having been £1,672 19*s.* 3*d.*

Professor Thorpe moved that the thanks of the Society be tendered to the Treasurer for his services during the past session; Dr. Perkin seconded the motion. Dr. Russell, after replying, proposed a vote of thanks to the auditors, Messrs. R. H. Davies, Friswell, and Rideal; this was seconded by Dr. P. F. Frankland, and acknowledged by Mr. Friswell.

Mr. J. Newlands proposed a vote of thanks to the Officers and Council, which was seconded by Dr. J. Voelcker, and acknowledged by Dr. Armstrong.

Professor Clowes moved that the thanks of the Fellows be tendered to the Editors, Abstractors, and Librarian for their important services during the year. Dr. Collie seconded the motion. Mr. Groves and Dr. Thorne replied.

Messrs. Foster and E. W. Voelcker having been appointed Scrutators, a ballot was taken, and as result the following were declared elected as Officers and Council for the ensuing session.

President: W. J. Russell, Ph.D., F.R.S.

Vice-Presidents who have filled the office of President: Sir F. A. Abel, C.B., D.C.L., F.R.S.; W. Crookes, F.R.S.; Warren de la Rue, D.C.L., F.R.S.; E. Frankland, D.C.L., F.R.S.; J. H. Gilbert, Ph.D., F.R.S.; J. H. Gladstone, Ph.D., F.R.S.; A. W. Hofmann, D.C.L., F.R.S.; H. Müller, Ph.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, Ph.D., F.R.S.; Sir Lyon Playfair, Ph.D., K.C.B., F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents: G. Carey Foster, F.R.S.; J. W. Mallet, M.D., F.R.S.; H. McLeod, F.R.S.; Ludwig Mond; J. Emerson Reynolds, M.D., F.R.S.; Robert Warington. F.R.S.

Secretaries: H. E. Armstrong, Ph.D., F.R.S.; J. Millar Thomson; F.R.S.E.

Foreign Secretary: F. R. Japp, LL.D., F.R.S.

Treasurer: T. E. Thorpe, B.Sc., F.R.S.

Ordinary Members of Council: Norman Collie, Ph.D.; A. H. Church; Frank Clowes, D.Sc.; Wyndham Dunstan; John Ferguson, M.A.; Charles W. Heaton; E. Kinch: H. F. Morley, M.A.; F. J. M. Page; S. U. Pickering, M.A.; R. T. Plimpton, Ph.D.; Thomas Purdie, B.Sc.

HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY, ST. MARTIN'S LANE.

Issued 11/4/1889.

ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 66. Session 1889–90.

April 4th, 1889. Dr. W. J. Russell, F.R.S., President, in the Chair.

Mr. Alexander Hill was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. William Waters Butler, Crown Brewery, Birmingham; and Francis Ransom, Hitchin.

The following were elected Fellows of the Society:—Messrs. John Leigh Hoskyns Abrahall; James Aunal; Richard Douglas Bailey; T. D. Collis Barry; Frederick William Boam; Harry Broadbent; Edward Barnwell Cook; Francis Edward John Cridland, Alexander Archie Cunningham; Thomas Hill Easterfield; Joseph T. Freestone; William Frew; James Hall; Richard Ashworth Hoyle; Henry Richardson Hoyles; Herbert Ingle; Clement Josep Leaper; George Cannon McMurtry; Christopher J. McNally, M.D.; James Bruce Miller; William Beattie Nesbitt, B.A.; George Thos. Wilkinson Newsholme; John Charles Platts; Charles Proctor; Arthur Avery Read; Ernest Reckitt; Duncan Taylor Richards; Richard Wrightwick Roberts; Thomas Alexander Shegog; Henry Simmonds; John William Slater; Henry Charles Anslie Vine; Walter Arthur Voss; William John Waterhouse; Patrick Alexander Weir, M.B.; John Tsawoo White; Charles Wood; Mortimor Woolf.

The following papers were read:—

33. "The rate of dissolution of metals in acids." By V. H. Veley.

When the rate of evolution of a gas is taken as the measure of the amount of interaction between metals and acids, the result is due to a variety of causes, each one of which is variable at any moment of

time, and its peculiar effect not susceptible of mathematical analysis. Among the varying conditions are the surface of the metal exposed, the local rise of temperature, the rate of diffusion of the metallic salt formed in the acid liquid and the rate of its removal by the gas-bubbles. In the present research metallic spheres by various mechanical devices were rolled about continuously and regularly within the acid liquid, and the products of the changes continuously removed from the immediate neighbourhood of the metal. The dissolution of copper in a solution of potassium bichromate acidified with sulphuric acid was investigated as affording a case in which no gas is evolved as such. The dependence of this action on the conditions of (i) temperature, (ii) proportion of sulphuric acid, and (iii) proportion of potassium bichromate is illustrated by various series of experiments.

(i.) As regards temperature, it is shown that if this be varied between 21° and 41° in an arithmetical proportion, the amount of chemical action varies in a geometrical proportion; in this respect the change is perfectly analogous to several others quite different from it and from one another. Attention is drawn to this relation as common to a number of chemical changes, and to the causes on which it is probably dependent. (ii.) On varying the amounts of sulphuric acid in an arithmetical proportion within the limits of 41·3 and 23·5 grams per litre, the amount of change also varies in an arithmetical proportion. (iii.) The amount of change is at first considerably increased by increase of proportion of potassium bichromate, but the effect gradually diminishes almost to *nil*, at which point the bichromate can be considered as so much inert material; the amounts used varied from 22·1 to 66·3 grams per litre.

34. "Note on the interaction of metals and acids." By Henry E. Armstrong.

When a metal forming an element in a voltaic couple is dissolved, the rate of dissolution is in accordance with Ohm's law, $C = E/R$: and this should apply also to the case in which a metal is dissolved without any precaution being taken to arrange it as an element of a couple, as the action is conditioned by the formation of, and takes place within, "local circuits." The changes attending the dissolution of metals may, therefore, in a certain sense be said to be purely electrical in the first instance; yet within recent years it has been argued by various chemists that the phenomena are only in part electrical and in part chemical—whatever this may mean. The author discusses the various phases of such changes, and criticises the conclusions arrived at by Spring and Aubel and others.

Discussion.

Referring to Mr. Veley's experiments, Dr. Armstrong expressed the opinion that the results were in no way commensurate with the labour expended in obtaining them: although by introducing bichromate polarisation by hydrogen had been prevented, its use had introduced complications which made the analysis of the results impossible; in fact the information likely to be obtained from such experiments was not of the kind required in the present state of chemical science. Thus the proof obtained that a copper sphere dissolved uniformly in a mixture of sulphuric acid and bichromate was but a proof of the efficiency of the stirring apparatus: such would necessarily be the case, as the values of E and R remained almost unchanged throughout the experiment owing to the relatively small proportion of the agents used up.

Mr. Veley, in the course of a reply in which he attempted to justify his position, mentioned that he had had occasion to verify Dr. Russell's observation that silver is not dissolved by nitric acid, to which reference had been made, and stated that in experiments with copper and nitric acid he had observed that the action took place at first more slowly and only attained a maximum rate when a certain small amount of nitrate was formed.

Dr. Armstrong remarked that this was a really important observation, proving that the dissolution of copper in nitric acid was dependent on the presence of a third substance—perhaps cupric nitrate. The discovery of the exact conditions which determine any particular chemical change is at the present time of great importance, and investigations establishing these were much required; it was useless, however, to study cases in which complications instead of simplifications were introduced, as even the changes which apparently were of the simplest kind were probably but the end results of more or less complex series of successive or simultaneous changes.

35. "A zinc mineral from a blast furnace." By J. Tudor Cundall.

The author has examined a mineral found in cavities of the wall of a blast furnace at Mostyn, in North Wales; it crystallises in white to yellow translucent tufts, of the relative density 5·60. Analysis gave results which show that it is impure zinc oxide:—

	ZnO.	Pb.	S.	SiO_2.	FeO.
I.	97·96	1·02	0·39	0·61	039
II.	98·79	0·95	0·10	trace	trace

It was examined crystallographically by Mr. A. Hutchinson, who found that the crystals belong to the rhomboidal system, and exhibit

combinations of the hexagonal prism and pyramids with the basal plane; two new forms were also noted, viz., the rhombohedron $r\{100\}$ and the hexagonal pyramid $h\{21, 13, 17\}$.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

A Treatise on Chemistry, by H. E. Roscoe and C. Schorlemmer. Vol. III, Organic Chemistry, Part V. From the Authors.

Results of Experiments at Rothamsted on the Growth of Potatoes for twelve years in succession on the same land, by J. H. Gilbert (Pamphlet). From the Author.

Chemical Lecture Notes, by P. T. Austen. New York 1888. From the Author.

Royal Agricultural College: Field Experiments. Barley; Pasture; by E. Kinch. Cirencester 1888 (Pamphlet). From the Author.

Experiments on the Composition of Coal, by W. Foster. London 1884 (Pamphlet). From the Author.

University Studies; published by the University of Nebraska. Vol. I, No. 2. Lincoln, Nebraska 1888. From the University.

II. *By Purchase.*

The Manual of Brewing, Scientific and Technical, by E. G. Hooper. Third Edition. London 1885.

FARADAY LECTURE.

The Faraday Lecture will be delivered on June 4th, by Professor Mendeleef, in the Theatre of the Royal Institution. The Fellows of the Society will entertain the Faraday Lecturer at a dinner at the Holborn Restaurant on the following evening.

At the next meeting, on April 18th, the following paper will be read:—

"Note on Naphthalene-derivatives." By Dr. Armstrong, and Messrs. Hiller, Holding, Percival, Rossiter, and Wynne.

HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY, ST. MARTIN'S LANE.

Issued 3/5/1889.

ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 67. Session 1889–90.

April 18th, 1889. Mr. W. Crookes, F.R.S., Vice-President, in the Chair.

Messrs. J. L. Hoskyns-Abrahall, D. Carmody, C. J. McNally, M.D., C. Proctor and W. J. Waterhouse were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. John Evans, care of Messrs. Savory and Moore, 86, King's Road, Brighton; William Taylor Gibbs, Richmond House, Plaistow, Essex; Byron B. Goldsmith, 19, East 74th Street, New York City, U.S.A.; Charles James Grist, West View, Grange Road, Egham; Alfred Edward Tibson, 79, South Hill Park, Hampstead Heath, N.W.; Ignatius Singer, Nailsworth, South Australia.

The following papers were read:—

36. "Sawarri fat." By J. Lewkowitsch, Ph.D.

Sawarri nuts contain 63 per cent. of a white solid fat, of which the author has determined the physical constants. The density is 0·8981 at 40° C. relatively to that of water at 15° C.; the melting point lies between 29·5° C. and 35·5° C.; the solidifying point at from 23·3° to 29° C. The acids from the fat melt at 48·3° C. to 50° C. and solidify at 47—46° C.

Saponification value (Köttsdorffer)	199·51	
Insoluble acids (Hehner's value)	96 91	p. c.
Glycerol determined by the acetin method	9·14	,,
Free acids	2·4	,,
Mean molecular weight of the acids	272 8	,,
Soluble acids (Reichert's value)	0·65	,,
Iodine value of the fat (v. Hübl)	49·5	,,

Iodine value of the acids	51·5	p. c.
Acetyl value (Benedikt)	77·5	„
Iodine value of the acetylised fatty acids	51·8	„

The author intends to examine the acids in the manner indicated by Hazura.

37. "Note on β-Phenylnaphthalene." By Watson Smith.

Zincke and Breuer (*Annalen*, **226**, 23—60) and Zincke (*ibid.*, **240**, 137—146) succeeded in synthesising β-phenylnaphthalene by the dehydration and condensation of styrolene alcohol:

$$2C_6H_5{\cdot}CH(OH){\cdot}CH_2(OH) - 4H_2O = C_6H_4{<}\begin{matrix}CH{:}CPh\\CH{:}CH\end{matrix}{>}.$$

β-Phenylnaphthalene melts at 101°, and is easily soluble in alcohol, ether, benzene and chloroform; on oxidation with chromic anhydride in glacial acetic acid solution it yields a quinone which crystallises in fine, bright-yellow needles, melting at 110°; this quinone possesses the characteristic property of rapidly polymerising on exposure of its solution to light, an insoluble polymeride being precipitated. In 1879 the author obtained a phenylnaphthalene by passing a mixture of bromobenzene and naphthalene through a red-hot tube (*Chem. Soc. Trans.*, 1881, 546), and for reasons then fully stated, he considered it to be β-phenylnaphthalene. Zincke attempted to obtain the hydrocarbon by the author's method, but seems to have failed, as he gives it as his opinion that it cannot be prepared in this way, or, that if a hydrocarbon is formed, it must be α-phenylnaphthalene. The author's attention was recently called to these facts, and especially to the latter statement by Professor Schorlemmer, and he was thus led to attempt the preparation of Zincke's quinone from some of a fairly abundant stock of phenylnaphthalene still remaining. The result was that the conversion into the quinone by Zincke's method proceeded with the utmost ease, a product answering in every respect to the quinone described by that chemist being obtained, amply confirming the author's earlier conclusion that the phenylnaphthalene obtained by him was the β-isomeride.

The author cannot understand that any such difficulty as Zincke describes should arise in preparing phenylnaphthalene by the pyrogentic method. Three products are principally obtained after removing excess of bromobenzene, viz., naphthalene, dinaphthyl and phenylnaphthalene; there may also be a minute quantity of diphenyl. Fractional distillation easily removes naphthalene and diphenyl, leaving phenylnaphthalene boiling at 345°, and dinaphthyl boiling above 440°. Boiling with somewhat dilute alcohol now extracts

phenylnaphthalene, and leaves behind dinaphthyl, which is insoluble in this liquid. Usually a second sublimation is necessary to obtain a product melting at 101°, that first obtained melting at about 96° C.

Discussion.

Dr. Armstrong remarked that it was most probable that the original product was the α-derivative; the proof now advanced that the hydrocarbon obtained by Mr. Watson Smith's method was the β-compound was of interest, as affording an indication that isomeric change of the α- into the β-derivative took place at high temperatures.

38. "Nitro-β-chloronaphthalene." By Henry E. Armstrong and W. P. Wynne.

β-Chloronaphthalene is readily nitrated by dissolving it in its own weight of glacial acetic acid and adding about $2\frac{1}{2}$ molecular proportions of nitric acid ($d = 1{\cdot}42$): the mixture is allowed to stand for two or three days. β-Bromonaphthalene behaves similarly. Nitro-β-chloronaphthalene crystallises from spirit in sulphur-yellow needles melting at 116°; on distillation with PCl_5 it yields the dichloronaphthalene melting at 63·5°, and is therefore the heteronucleal 1 : 2′ α-nitro-β-chloronaphthalene. On reduction it yields the corresponding amidochloronaphthalene. The authors are studying the sulphonic acids derived from this amine.

39. "The action of halogens on betanaphthol." By Henry E. Armstrong and E. C. Rossiter.

If betanaphthol be treated with a single molecular proportion of bromine it is converted, as shown by Smith, into a homonucleal monobromo-derivative which presumably corresponds in constitution with 1 : 2 chlorobetanaphthol; if an excess of bromine be used, a tetrabromonaphthol is produced, and as this yields bromophthalic acid on oxidation, it contains one of its four bromine atoms in the second nucleus. The authors have sought to determine at what stage the bromine atom becomes introduced into the second nucleus.

By treating betanaphthol with two molecular proportions of bromine it is almost entirely converted into dibromobetanaphthol; this crystallises from acetic acid with one molecular proportion of the acid in prisms melting at 84°; the acid of crystallisation is spontaneously given off on exposure of the crystals. The pure substance crystallises from petroleum spirit in woolly needles melting at 106°. On

oxidation with alkaline permanganate it yields bromophthalic acid: whence it follows that on introducing a second atom of bromine into betanaphthol it enters the non-hydroxylised nucleus.

The preparation of a tribromonaphthol appears to present difficulties, a mixture of di- and tetra-derivatives being usually obtained. Together with the bromonaphthols, relatively small amounts of yellow products are always formed, which probably correspond to the chlorinated keto-compounds described by Zincke.

When betanaphthol is submitted to the action of a single molecular proportion of chlorine, it yields but a relatively small amount of chlorobetanaphthol, the chief product being a resinous substance (Cleve); this result has found an explanation in Zincke's experiments, which show that chlorine tends to convert betanaphthol into additive keto-compounds. The authors find that a theoretical yield of chlorobetanaphthol (m.p. 69°) is obtainable by gently warming betanaphthol suspended in thrice its weight of carbon bisulphide with a molecular proportion of sulphuryl chloride, SO_2Cl_2. On attempting to prepare dichlorobetanaphthol by further treatment with SO_2Cl_2, little besides resinous matter was obtained; alphanaphthol, in like manner, when submitted to the action of two molecular proportions of the chloride, afforded a large amount of resinous matter. Chlorobetanaphthol is almost entirely converted by a single molecular proportion of bromine into a bromochlorobetanaphthol corresponding to the dibromobetanaphthol previously described. It also crystallises with one molecular proportion of acetic acid in long prismatic needles melting at 92°; the pure substance sublimes in fine needles melting at 101°, but does not crystallise satisfactorily from any solvent.

Schaeffer's betanaphtholsulphonic acid is converted by bromine into a monobromo-derivative, which may also be obtained by sulphonating Smith's bromobetanaphthol (Armstrong and Graham); the corresponding chloro-acid is readily formed on sulphonating chlorobetanaphthol, together with a small quantity of an isomeric acid yielding more soluble salts. The brom- and chlor-acids behave alike on treatment with excess of bromine, being converted into the bromhydroxynaphthaquinonesulphonate, $C_{10}H_3BrO_2(OH)\cdot SO_3H$, first described by Armstrong and Graham; a relatively very small proportion of dibromhydroxynaphthaquinone being also produced. Armstrong and Graham came to the conclusion that the bromhydroxysulphonate—which contains the bromine in the quinonic nucleus—was the final product of the action of bromine, but later experiments have shown that this is only the case when the experiment is made by treating Schaeffer's salt with bromine; if the pure bromhydroxyquinonesulphonate be used instead, the quinonic nucleus becomes destroyed and a sulphophthalic derivative is obtained. The hydrogen bromide

produced in the formation of the quinonesulphonate from Schaeffer's salt, in fact, protects the former from oxidation.

Armstrong and Graham succeeded in obtaining only a small quantity of a dibromo-derivative from Schaeffer's acid, the tendency being for the action to extend at once to the formation of the quinone-sulphonate; by brominating a solution of the potassium salt of Schaeffer's acid in muriatic acid, Armstrong and Streatfeild succeeded, however, in preparing a tribromo-derivative. Both the di- and the tri-bromo-acid gave easily soluble salts, and, as on treatment with bromine, they were converted into quinonesulphonate, the bromine atoms are contained in the hydroxylised nucleus. By sulphonating the above-described bromochloro- and dibromo-betanaphthols, the authors have obtained sulphonic acids, the salts of which are difficultly soluble and which, on treatment with bromine, yield a large proportion of the dibromhydroxynaphthaquinone already mentioned; the production of this compound is confirmatory of the heteronucleal constitution of the two di-derivatives of betanaphthol. Bromochlorobetanaphthol yields two isomeric acids on sulphonation; it is noteworthy that neither these nor the acid from the dibromo-compound yield Schaeffer's acid on reduction; as this acid is obtained on reducing the acids produced on sulphonating chloro- and bromo-betanaphthol, it follows that the sulphonation of the mono- and di-derivatives of betanaphthol takes place in a different manner—it may be that, as in the case of betanaphthol, a sulphate is first produced, and that the subsequent isomeric change takes a different course; or perhaps a sulphate is formed in the case of the mono-derivative, while direct sulphonation is affected in that of the di-derivative. The authors are engaged in further investigating the sulphonic acids of the chloro- and bromo-naphthols generally.

40. "β-Methoxynaphthalenesulphonic acids." By J. Percival, B.A.

It has been shown by Armstrong and Amphlett that if β-ethoxynaphthalene be sulphonated by means of chlorosulphonic acid without application of heat a mixture of two sulphonic acids is obtained, one of which corresponds to Schaeffer's betanaphtholsulphonic acid; and that if the product be heated on the water-bath for a short time this latter acid is alone obtained, an isomeric change taking place. The author has undertaken a series of experiments with the object of determining whether any effect is produced by varying the radicle introduced in place of the hydroxylic hydrogen of betanaphthol; in the first instance he has studied the behaviour of β-methoxynaphthalene prepared from betanaphthol, and finds that there are

very marked differences to be observed in the behaviour of the methoxy- and ethoxy-compounds.

The product obtained without application of heat chiefly consists of an unstable acid together with a relatively small proportion of a stable acid corresponding to Schaeffer's betanaphtholsulphonic acid; but after heating during a couple of hours on the water-bath the unstable acid is no longer present, having undergone isomeric change into the stable acid. If the aqueous solution of the unstable acid be heated nearly to boiling, the acid is decomposed, β-methoxynaphthalene separating; in this way it is easy to ascertain the amount of unstable acid in the original product of sulphonation. Even a solution of the barium salt of the unstable acid gradually undergoes decomposition when evaporated, β-methoxynaphthalene and barium sulphate becoming separated. No such behaviour was noticed in the case of the barium salt of the unstable ethoxy-acid, although this salt was observed to decompose at about the temperature at which the water of crystallisation was expelled, 130—140°. On adding bromine to a solution of the unstable methoxy-acid, a precipitate is at once formed consisting of tribromo-β-methoxynaphthalene; this crystallises from benzene, in which it is very soluble, in long, slender, white needles melting at 105°; no such precipitate is obtained from the unstable ethoxy-acid.

The salts of the unstable acid are very soluble, the potassium salt crystallising in plates, which aggregate into nodular masses, containing half a molecular proportion of water. The salts of the stable acid are difficultly soluble; like the corresponding ethoxy-acid, it is readily converted by bromine into a bromo-β-methoxysulphonate and ultimately into bromhydroxyquinonesulphonate identical with that obtained from Schaeffer's acid.

41. "The acids formed by displacing NH_2 in Brönner's betanaphthylaminesulphonic acid by halogens." By W. Houlding, B.Sc.

Arnell has shown that two isomeric acids are formed on sulphonating β-chloronaphthalene, and subsequent experiments by Forsling and others have proved that these acids correspond to the Badische and Brönner modifications of betanaphthylaminesulphonic acid; the 1 : 2′ acid is the chief product and the 2 : 3′ acid the minor product, especially if chlorosulphonic acid be employed as sulphonating agent. Armstrong and Wynne have shown that although the minor product when heat is not applied, the 2 : 3′ acid becomes the major product if after sulphonation the crude acid be heated during several hours at 150—160°; and they have consequently suggested that the 2 : 3′ acid is not a direct product of sulphonation but results entirely from the

occurrence of isomeric change. β-Bromo-and β-iodo-naphthalene were each found in like manner to afford two isomeric acids, which it was to be presumed corresponded to those obtained from β-chloronaphthalene, but Armstrong and Wynne have pointed out as noteworthy that the melting point of the sulphochloride of the iodo-acid obtained as minor product was abnormally low, thus—

	Chlorosulphochloride.	Bromosulphochloride.	Iodosulphochloride.
Major product	130°	147°	174°
Minor ,, ...	109	125	92·5

The author has therefore carefully compared the acids prepared from Brönner's 2 : 3′ betanaphthylaminesulphonic acid with those obtained by sulphonating β-chloro-, β-bromo- and β-iodo-naphthalene. As was to be expected, his results entirely confirm those of Forsling with reference to the identity of the chloro-acid from Brönner's acid with the minor product of sulphonation of β-chloronaphthalene—that which affords a sulphochloride melting at 109°. It is noteworthy that both the chlorosulphochloride and the chlorosulphobromide, m. p. 124°, yield the same sulphonamide melting at 183°, which is a proof of the non-occurrence of an isomeric change such as was observed by Gessner in the case of α-bromonaphthalenesulphonic acid. In like manner, the author finds that the bromo-acid from Brönner's acid is identical with the minor product of sulphonation of β-bromonaphthalene: the salts of the acids are similar in appearance to those of the corresponding chlor-acid, and are also all anhydrous; the sulphochloride melts at 124°; the sulphobromide at 118°: both sulphochloride and bromide yield the same sulphonamide, melting at about 204°. By distilling the bromosulphochloride with PCl_5 it is converted into a chlorobromonaphthalene, which crystallises in thin plates, melting at 137°; the corresponding dibromonaphthalene was obtained in small needles melting at 149°, but owing to the small amount at disposal this melting point cannot be regarded as sufficiently determined. The iodo-acid obtained from Brönner's acid was found to differ considerably from that obtained as minor product on sulphonating β-iodonaphthalene, the sulphochloride melting at 140° instead of 92·5°, and the sulphonamide at about 220° instead of 211°; the salts of the two acids also differ, the barium and sodium salts of that from Brönner's acid crystallising both in anhydrous plates and in monohydrated needles.

It appears therefore that on sulphonating β-iodonaphthalene either the initial change is the same as that which occurs on sulphonating the chloro- and bromo-compounds, and the consequent isomeric change follows a different course; or sulphonation is perhaps simultaneously

effected in two different ways, neither iodo-acid being the product of isomeric change.

With the object of determining the nature of the change, experiments have been instituted with the iodo-acids corresponding to the three amido-acids isomeric with Brönner's; the results will form the subject of a subsequent communication.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Notes on Analytical Chemistry for Students in Medicine, by A. J. Bernays. Third Edition, London 1889. From the Author.

The Agricultural Value of Sulphate of Ammonia, by R. Warington. London 1889 (Pamphlet). From the Author.

Royal Gardens, Kew: Bulletin of Miscellaneous Information. Vol. I, 1887; Vol. II, 1888; Vol. III, parts for Jan.—April, 1889. From the Director, Royal Gardens, Kew.

On the Serpentine of Montville, New Jersey, by G. P. Merrill. (From the Proc. of the U.S. National Museum). Washington 1889. (Pamphlet.) From the Author.

FARADAY LECTURE.

The Faraday Lecture will be delivered on June 4th, by Professor Mendeleef, in the Theatre of the Royal Institution. The Fellows of the Society will entertain the Faraday Lecturer at a dinner at the Holborn Restaurant on the following evening.

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Issued 10/5/1889.

ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 68. Session 1889–90.

May 2nd, 1889. Dr. W. J. Russell, F.R.S., President, in the Chair.

Messrs. G. C. McMurtry and H. H. Robins were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. George William Howard, 3, Monson Terrace, Tunbridge Wells; Edward Wightman Bell, Spalding; Frederick Charles Knight, Trinidad, Colorado, U.S.A.; D. O'Mahoney, Queen's College, Cork; Benjamin Phillips, Oriental Bank Buildings, Bombay; Emanuel Roberts, Moratua, Ceylon; Robert M. W. Swan, 15, Walmer Crescent, Glasgow.

The following papers were read:—

42. "Thiophosphoryl fluoride." By T. E. Thorpe, F.R.S., and J. W. Rodger, Associate of the Normal School of Science, South Kensington.

This gas, the existence of which was announced by the authors in 1888 (*vide* Trans., **53**, 766), may be made by the action of arsenic trifluoride on thiophosphoryl chloride, or by heating a mixture of bismuth trifluoride, or better, lead fluoride, with phosphorus pentasulphide.

As the gas is readily acted on by the air or by moisture, and is decomposed at a moderately high temperature, it is necessary to take certain precautions in the preparation if it is wished to obtain it pure. The air in the apparatus should be displaced by dry nitrogen, and the mixture should be heated in a leaden vessel to a temperature not

exceeding 250°. The gas has no action on dry mercury, and may be stored in a glass gas-holder.

Analyses and determinations of its vapour-density showed that it possesses the formula PSF_3.

It is a transparent, colourless gas, which under a pressure of 10 to 11 atmospheres at ordinary temperatures, condenses to a colourless, mobile liquid.

It is spontaneously inflammable in air, burning with a greyish-green flame, forming phosphorus pentafluoride, phosphorus pentoxide, and sulphur dioxide, thus: $10PSF_3 + 15O_2 = 6PF_5 + 2P_2O_5 + 10SO_2$, and spontaneously explodes with oxygen.

When heated or subjected to electric sparks, it is decomposed with separation of sulphur and phosphorus, and formation of phosphorus trifluoride, and eventually phosphorus pentafluoride. If the heating is effected in a glass tube at a sufficiently high temperature, the gas is ultimately converted into silicon tetrafluoride.

It has no action on oil of vitriol, carbon bisulphide, or benzene. It is soluble to some extent in ether; the solution burns with a greenish flame. Water gradually decomposes it, forming sulphuretted hydrogen, phosphoric acid and hydrogen fluoride, $PSF_3 + 4H_2O = H_2S + H_3PO_4 + 3HF$.

On shaking the gas with a moderately strong solution of alkali, it is absorbed with the formation of a thiophosphate and a fluoride. Thus with caustic soda, $PSF_3 + 6NaOH = Na_3PSO_3 + 3NaF + 3H_2O$.

The gas combines with gaseous ammonia to form a solid product, in accordance with the equation $PSF_3 + 4NH_3 = 2NH_4F + P(NH_2)_2SF$, and the product is acted on by water, thus: $2NH_4F + P(NH_2)_2SF + H_2O = 2(NH_4F)HF + P(NH_2)_2HSO$, forming ammonium fluoride, hydrogen fluoride, and thiophosphodiamic acid. On treating the solution with copper sulphate, copper sulphide is ultimately formed, and the filtered liquid gradually deposits a crystalline salt of a bluish-green colour, consisting of a double phosphate and silicofluoride of copper, $Cu_3P_2O_8{\cdot}CuSiF_6$.

43. "The boiling point of sodium and potassium." By E. P. Perman.

Sodium and potassium were boiled in a hollow iron ball, which was heated by means of a blowpipe; the temperature was found in each case by means of an air thermometer, consisting of a glass bulb with a capillary stem which was lowered into the vapour, sealed, and broken open under water. The mean result for sodium was 742°, and for potassium 667°.

44. "Note on the heat of neutralisation of sulphuric acid." By S. U. Pickering.

The heat of neutralisation is affected by the proportion of water present, and this latter should, theoretically, be infinite. By means of Thomsen's determinations of the heat evolved on diluting the solutions concerned, we can calculate approximately the values of the heat of neutralisation in infinity of water. The values for 2HCl and H_2SO_4 thus become 27,416 and 30,477 cal., instead of 27,480 and 31,380 cal., as they are when 200 H_2O is present; but Thomsen's results on the dilution of sulphuric acid were not extended sufficiently to show an abrupt change which occurs at the extreme end of the curve, and, when the correction is deduced from a more extensive series of experiments which the author has performed, the value for sulphuric acid becomes reduced to 28,197 cal., a value within experimental error, the same as that of hydrogen chloride.

45. "α-ω-Diacetylpentane, and α-ω-Dibenzoylpentane." By F. Stanley Kipping, Ph.D., D.Sc., and W. H. Perkin, jun., Ph.D.

Acetobutylbromide and ethylic sodacetoacetate interact readily when warmed together in alcoholic solution with formation of ethylic α-ω-diacetylcaproate, $COMe{\cdot}(CH_2)_4{\cdot}CH(COMe){\cdot}COOEt$. This compound is a colourless oil, boiling at 238—242° (220 mm.); when treated with an absolute alcoholic solution of ammonia, it yields a crystalline compound, $C_{10}H_{15}NO_2$, melting at about 235° with partial decomposition. It is readily hydrolysed by warm, alcoholic potash, yielding α-ω-diacetylpentane, together with smaller quantities of ω-acetylcaproic acid and acetic acid.

α-ω-Diacetylpentane, $COMe{\cdot}(CH_2)_5{\cdot}COMe$, crystallises in waxy plates, melts at 48—49°, and boils at about 213° (under 300 mm. pressure) without decomposition. It combines with hydrogen sodium sulphite, forming a waxy, seemingly amorphous compound, which is decomposed when warmed with water.

By treating the diketone in the cold with excess of hydroxylamine hydrochloride and potassium carbonate, it is converted into the dihydroxime, $CMe(NOH){\cdot}(CH_2)_5{\cdot}CMe{:}NOH$; this separates from a mixture of benzene and light petroleum in the form of a crystalline powder, melting at 84—85°.

ω-Acetylcaproic acid, $COMe{\cdot}(CH_2)_5{\cdot}COOH$, crystallises in colourless plates, melts at 29—30°, and, when pure, distils under reduced pressure with only slight decomposition. The silver salt, $C_8H_{13}O_3Ag$, crystallises from boiling water in colourless plates.

By warming an alcoholic solution of acetobutylbromide with

ethylic sodomethylacetoacetate, ethylic α-methyl-α-ω-diacetylcaproate. $COMe\cdot(CH_2)_4\cdot CMe(COMe)\cdot COOEt$, is obtained as a colourless oil, boiling at 255—260°, (200 mm.). It yields α-methyl-α-ω-diacetyl pentane, $COMe\cdot(CH_2)_4\cdot CMeH\cdot COMe$, when hydrolysed with alcoholic potash.

Ethylic α-ω-dibenzoylcaproate, $COPh\cdot(CH_2)_4\cdot CH(COPh)\cdot COOEt$, is obtained by treating benzoylbutylbromide with ethyl sodobenzoylacetate in alcoholic solution. It is quickly hydrolysed when boiled with alcoholic potash, yielding α-ω-dibenzoylpentane, ω-benzoylcaproic acid, and benzoic acid.

α-ω-Dibenzoylpentane, $COPh\cdot(CH_2)_5\cdot COPh$, crystallises from dilute methyl alcohol in long needles, melting at 67—68°. The dihydroxime, $CPh(NOH)\cdot(CH_2)_5\cdot CPh{:}NOH$, prepared by treating an alcoholic solution of the diketone at the ordinary temperature with hydroxylamine hydrochloride and potash, crystallises from methyl alcohol in small, glittering needles, and melts at 175—176°.

ω-Benzoylcaproic acid, $COPh\cdot(CH_2)_5\cdot COOH$, crystallises from light petroleum in long, transparent plates, melting at 81—82°. The silver salt, $C_{13}H_{15}O_3Ag$, is a colourless, seemingly amorphous compound, almost insoluble in water.

The authors are at present engaged in investigating the behaviour of diacetyl- and dibenzoyl-pentane towards reducing and dehydrating agents. Very interesting results have been obtained, an account of which they hope to be able to lay before the Society at an early date.

46. "Acetopropyl- and acetobutyl-alcohol." By Harold G. Colman, M.Sc., Ph.D., and W. H. Perkin, jun.

In a previous communication to the Society (Trans., **51**, 702) it was shown by one of the authors that acetobutylalcohol, obtained by boiling methyldehydrohexonecarboxylic acid with water, differs very widely from the substance of that name previously obtained by Lipp (*Ber.*, 1885, 3280) by boiling ethylic ω-bromopropylacetoacetate with dilute aqueous hydrogen chloride: the boiling point of the former being 227°, whereas the latter product distilled at 154—155°—a difference of 70°.

In a paper published some time since (*Ber.*, 1888, 2138) "On the Action of Sodium on Ethylic Monochloracetate," Fittig and Erlenbach, in describing a substance boiling at 128°, which they supposed to be acetoisopropylalcohol, took occasion to state that the acetobutyl- and acetopropyl-alcohols previously described by the authors, could not possibly have the constitution assigned to them—owing to their syrupy consistency and high boiling points—and that the description given by Lipp of his acetobutylalcohol agreed much better with the pro-

perties such a substance might be expected to possess. In a later paper (*Ber.*, 1888, 2647) these chemists discovered that their compound was not acetoisopropylalcohol, but was simply acetolethyl ether, $CH_3 \cdot CO \cdot CH_2 \cdot OC_2H_5$. As, however, in spite of this they did not withdraw their previous remarks on the nature of acetobutyl- and acetopropyl-alcohol, and as the authors had extensively used these substances in the synthesis of ring-derivatives, and drawn important theoretical conclusions from the results obtained, they have thought it necessary to again carefully examine these alcohols with a view to further establishing their identity.

In the first place they carefully repeated Lipp's experiment and found that the acetobutylalcohol obtained by him did in reality contain a considerable quantity of this substance, and that the product on distillation apparently boiled at 154—155°. Subsequent experiments showed, however, that this temperature, instead of being the boiling point, was in reality the decomposing point of the alcohol; the reason for this being, that the slightest trace of impurity is sufficient to prevent acetobutylalcohol from distilling without the most rapid decomposition into its anhydride (methyldehydrohexone) and water, the thermometer remaining constant at 154—155°. Lipp's acetobutylalcohol, when not too impure, can be distilled with slight decomposition under reduced pressure; the boiling point noticed in two cases being 157° under 100 mm. pressure, and 171° under 177 mm. pressure; on distilling acetobutylalcohol from methyldehydrohexonecarboxylic acid under the same conditions, almost identical boiling points were noticed.

Pure acetobutylalcohol was obtained from Lipp's crude product by distilling with steam, fractioning the methyldehydrohexone thus obtained, and dissolving it in water. In this way a thick oil was obtained which distilled under ordinary pressure at 225—227°, and was in every respect identical with the acetobutylalcohol from methyldehydrohexonecarboxylic acid.

These and other experiments, an account of which will be given later on, prove conclusively that acetobutyl alcohol, when pure, boils at 225—227°, and not at 154—155° as stated by Lipp. Acetopropylalcohol behaves in every respect, physically as well as chemically, as the lower homologue of acetobutylalcohol, and as this substance gives levulinic acid on oxidation, no further experiments in proof of its constitution are necessary.

At the next meeting, on May the 16th, there will be a ballot for the election of Fellows, and the following papers will be read:—

"The magnetic rotatory power of some nitrogen compounds." By Dr. W. H. Perkin, F.R.S.

"Frangulin." By T. E. Thorpe, F.R.S., and H. H. Robinson.

FARADAY LECTURE.

Professor Mendeleeff's lecture will be on the Periodic Law of the Chemical Elements; it will be delivered in the theatre of the Royal Institution, Albemarle Street, W., on Tuesday, June 4th, at 8.30 P.M. Fellows requiring additional tickets for the Faraday Lecture are requested to apply to Mr. Hall. The tickets are available for ladies.

The dinner at which the Fellows will entertain Professor Mendeleeff will take place at the Holborn Restaurant on Wednesday, June 5th, at 7 P.M. Tickets may be obtained from Mr. Hall. price half-a-guinea, not including wine.

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Issued 23/5/1889.

ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 69. Session 1889–90.

May 16th, 1889. Dr. W. J. Russell, F.R.S., President, in the Chair.

Messrs. C. Heinrich Trinks and Ernest F. Ehrhardt were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. William D. Cargill, B.Sc., Longhaugh, near Dundee; Henry W. Morrow, B.S., Wilmington, Delaware, U.S.A.; and Robert Redwood, 85, Gracechurch Street, E.C.

The following were elected Fellows of the Society:—William Taylor Gibbs, Byron B. Goldsmith, Charles James Grist, John Kitchin, John Edmund Legg, Francis Ransom, Alfred Edward Sibson, Ignatius Singer, Walter J. Sykes, William Virtue.

The following papers were read:—

47. "The magnetic rotation of nitrogen compounds." By W. H. Perkin, Ph.D., F.R.S.

In previous communications the author has shown that in the magnetic field the plane of polarisation of light is rotated to a greater extent in unsaturated than in saturated carbon compounds; in the present communication it is shown that in the case of nitrogen compounds the magnetic rotation is in like manner correlated with changes in the valency of the nitrogen.

Nitrates, nitrites and nitro-compounds.—The specific rotation of all these is low, thus:

Nitric acid	1·180
Methylic nitrate	2·057
Ethylic „	3·084
Propylic „	4·085
Isobutylic „	5·180
Ethylenic „	3·768
Glyceric „ (nitro-glycerin)	5·405
Isobutylic nitrite	5·510
Nitromethane	1·858
Nitroethane	2·837
Chloropicrin	5·384

The change attending the conversion of nitric acid into an ethereal salt is comparable with that of the acids of the acetic series into ethereal salts, the increase in the value for the nitrate being less than may be expected from the change in composition; thus:

Methylic nitrate ...	2·057	Methylic formate ..	2·495
Nitric acid.....	1·180	Formic acid	1·671
	0·877		0·824

Usual value of CH_2 1·023

The high rotation of isobutylic nitrite in comparison with that of the corresponding nitrate is an illustration of the influence exercised by unsaturated nitrogen; it is also noteworthy that the rotation of chloropicrin is less than that of chloroform (5·559).

Amines.—Very nearly the same value is obtained for ammonia, whether aqueous or alcoholic solutions be taken, the former giving 1·81, the latter 1·826; the aqueous solution examined contained 31 per cent., the alcoholic 14·48 per cent. NH_3: hence it would appear that little, if any, combination takes place between the ammonia and the solvent. Similar observations made with mixtures of equal volumes of isobutylamine and water or alcohol, and with a mixture of piperidine and water in the proportions $C_5H_{11}N : OH_2$, indicate, however, that combination takes place to some extent in these cases, the found and calculated values being as follows:—

	Calculated.	Found.	Difference.
Isobutylamine and water..	11·200	11·099	0·101
„ and alcohol.	10·459	10·361	0·098
Piperidine and water „...	6·810	6·724	0·086

The effect of hydrocarbon radicles on amines was studied in the following cases:—

Ethylamine	3·609
Diethylamine	5·662
Triethylamine	8·518
Propylamine	4·563
Dipropylamine	7·549
Tripropylamine	11·664
Isobutylamine	5·692
Diisobutylamine	9·936
Allylamine	5·587
Pentamethylenediamine	7·491
Aniline	16·162
Methylaniline	19·629
Dimethylaniline	22·823
Piperidine	5·810
Pyridine	8·761

From these numbers it will be seen that the effect of introducing a single radicle into ammonia is somewhat less than corresponds to a similar change in homologous series, viz., 1·023 per CH_2. The rotation is increased proportionally more by the displacement of a second hydrogen atom, and in the paraffinoid amines a very remarkable increase attends the introduction of the third radicle, indicating a marked difference to exist between secondary and tertiary amines. The effect of methyl in aniline is also very remarkable, the increase in the rotation being more than three times that which usually follows such an alteration in empirical composition in paraffinoid compounds. The value for piperidine is very low, and is in accordance with the conclusion that it is a saturated compound; the value for pyridine is also low in comparison with aniline and benzene (11·297).

The study of the salts of the amines has afforded noteworthy results: instead of the diminution which usually attends the formation of compounds, it is found that the observed rotation is slightly in excess of that calculated by adding the rotations of the constituent compounds in the case of the following "ammonium" chlorides:—

	Found.	Calculated.	Difference.
Ammonium chloride	6·096	6·032	+0·064
Ethylammonium chloride	7·997	7·823	+0·174
Diethylammonium chloride	9·896	9·876	+0·020
Piperidinium „	10·034	10·024	+0·010

Triethylamine, however, behaves "normally," and a normal result is also obtained in the case of ammonium nitrate and sulphate, thus:

	Found.	Calculated.	Difference.
Triethylammonium chloride	11·724	12·732	−1·008
Ammonium nitrate.....	2·316	2·998	−0·686
„ sulphate.....	4·963	5·951	−0·988

From the discussion of his results generally, the author arrives at the conclusion that in compounds of unsaturated "triad" nitrogen, the nitrogen has a greater influence than when it is present in the saturated condition, the difference in the values being about 0·5; this is only about half the difference usually observed on comparing the rotations of carbon compounds differing by 2H.

Discussion.

Dr. Gladstone said that the general result of Dr. Perkins' work, establishing a difference in nitrogen according as it is present in the saturated or unsaturated condition, was in accordance with the conclusion which he had arrived at from the study of refractive power; the peculiarities brought out by the study of the magnetic behaviour, however, were chiefly indicated by peculiarities in dispersive power, being less obvious in the refraction equivalents.

Professor Ramsay said that he should like, on some future occasion, to raise a discussion on the method adopted by Dr. Perkin and Dr. Gladstone in dealing with their results. He thought that the method followed by Schroeder in discussing volume constitution was perhaps applicable, and at all events was deserving of attention.

48. "The nature of solutions, as elucidated by a study of their densities, electric conductivities, heat capacity and heat of dissolution." By S. U. Pickering.

The solutions which form the subjects of this research are those of calcium chloride, calcium nitrate and sulphuric acid. The results obtained with the first of these have already been brought before the Society (Proc., 1888, 35), and tended to show that the curves representing the densities and heat of dissolution of solutions of different strengths, though apparently regular on a superficial inspection, are not really so; when they are analysed by differentiation they are resolved into a series of curves or straight lines, showing that breaks occur in the original curves; these breaks, moreover, correspond to hydrates of definite composition. The densities gave a series of straight lines on the first differentiation, bearing out Mendeleef's statement that such was the nature of the density curves in the case

of sulphuric acid and alcohol, whereas the heat of dissolution required two differentiations before it gave straight lines.

With calcium nitrate the determinations which have been made are much more numerous, and the results obtained are of a nature precisely similar to those with calcium chloride. The straight lines formed by the first differential coefficient of the densities are in this case inclined to each other so very slightly, as scarcely to warrant the conclusion that the whole figure is not a continuous curve, were it not that the heat results confirm in every detail the breaks which the rectilineal drawing of the density differential shows. The heat capacities (specific heat) of very weak solutions of this salt have also been determined, and they are found to afford a rectilineal figure indicating breaks at the same points as those deduced from the density and heat results.

The author has proceeded to an extensive examination of sulphuric acid solutions. On plotting out the first differential of his density results, he was surprised to find that it formed an irregularly curved figure, and not the rectilineal figure given by Mendeleef, and he was still more surprised to find that on plotting out the values used by Mendeleef himself, the figure obtained was curvilinear like his own, and not rectilinear like Mendeleef's. This led him to plot out Mendeleef's values for the first differential of the densities of alcohol, and in this case also he found that they gave an irregular curve, and not the rectilineal figure depicted by Mendeleef in this Journal (Trans., 1887, 780). Mendeleef's statement, therefore, that he had proved the hydrate theory by showing that the densities differentiated into straight lines meeting at points corresponding to definite hydrates is erroneous.

On applying a second differentiation to his density results with sulphuric acid the author obtained a series of straight lines, so that the density curve in this case resembles the heat curves in the case of the two calcium salts, and it is probable that the densities of these latter salts give rectilineal figures on the first differentiation only, because the constituent lines are straight within experimental error, and not because they are straight in reality.

The author has made determinations with a series of sulphuric acid solutions at four different temperatures, 8°, 18°, 28°, and 38°. The results obtained and the breaks shown were the same in every case, and the latter were found to become more apparent as the temperature is lower. The same conclusions as to the effect of a lowering of temperature in intensifying the change in general direction of the curve may be drawn from Mendeleef's determinations with alcohol at different temperatures.

Crompton's interpretation of Kohlrausch's determinations of the

electric conductivity of sulphuric acid solutions is next discussed. The author agrees with Crompton's conclusion that they give a rectilineal figure after two differentiations, but he differs from him in some of the details as to where the breaks occur, and shows that the most probable positions of these breaks agree very closely with those shown by his own density results.

The heat capacity of sulphuric acid solutions up to a strength of 12 per cent. was next determined, and the results were found to form a series of very slightly curved lines indicating breaks very clearly at the same points as did the densities. The original curves probably require two differentiations before they are reduced to straight lines.

The determination of the heat of dissolution of sulphuric acid solutions with the requisite degree of accuracy presented considerable difficulties, owing to the large amount of heat evolved. The results obtained confirmed the author's conclusions as to the nature of the heat curves in the case of the calcium salts. The whole curve was found to be made up of a series of independent curves, each of which gave a straight line on two, or, sometimes, on one differentiation, and the breaks agree in position with those deduced from the other properties. Although Thomsen's determinations of the heat of dissolution of sulphuric acid are far too few in number to prove the real nature of the curve, the author shows that they are quite sufficient to disprove the perfect regularity which Thomsen and his followers attribute to the interaction. Some marked changes are shown by it, and Thomsen's equation which is supposed to represent the curve so faithfully, is applicable, in reality, to but 1 per cent. of the whole figure.

The various hydrates which are proved by this work to exist in solution are numerous and complex. Those which calcium chloride forms contain 6, 7, 8, 10, 13, 18, 28, 86, and 1500 H_2O; calcium nitrate gives hydrates with 3, 3·5, 4·5, 5, 6, 10, 17, 51, 265, and 1810 H_2O; while with sulphuric acid we find hydrates with $\frac{1}{6}$, $\frac{1}{3}$, $\frac{2}{3}$, 1, $\frac{3}{2}$, 2, 4, 5, 9, 13, 24, 52, 135, 510, 1430, and 4950 H_2O. The existence of these is, naturally, more doubtful in some cases than in others, and it is impossible to determine the exact molecular composition when more than about $10H_2O$ is present. In some cases the hydrates of sulphuric acid have been established by six independent set of results obtained from the study of four distinct properties.

The excessively large amount of water present in the highest hydrate is a matter of especial interest, and the existence of such compounds explains the influence which mere traces of one substance may have on another substance (*e.g.*, impurities in metals). The highest hydrate of sulphuric acid contains only 0·1 per cent. H_2SO_4, yet the breaks at the extreme ends of the curve are comparatively

more marked and more certain than most of the others. The author has recently given a striking proof of the existence of the break in the heat curve of sulphuric acid at 0·3—0·4 per cent., in the fact that the heat of neutralisation of this acid becomes "normal" when this break is recognised.

The progress of differentiation was always applied to the experimental numbers themselves in the first case, but, for the second differentiation it was necessary, owing to the magnitude of the experimental error, to take the smoothed first differential curves, and not the experimental numbers. With the heat results, where the error is comparatively large, the first differentiation was performed on the curve representing the results as well as on the experimental numbers.

The author mentions a striking proof that the character of the second differential is not attributable to any peculiarity in the manner in which he drew the first differential figure from which it is deduced. When the contraction produced on mixing sulphuric acid and water in different proportions is plotted out, a figure results utterly unlike that representing the densities, and the first differential figure (obtained from the experimental numbers) which it gives is also quite unlike the first differential from the densities, yet these two dissimilar figures give on a second differentiation figures which are identical with each other, both as to the inclination of the straight lines of which they are composed, and as to the points at which these straight lines meet.

It may be noted that the maximum contraction on mixing sulphuric acid and water does not occur at a point corresponding to $H_2SO_4,2H_2O$, as has hitherto been supposed, but at a point some 4 per cent. below it, a point which is not coincident with any break.

The final conclusion which the author deduces from his work is the absolute rejection of any theory of dissolution other than the hydrate theory.

49. "The expansion of water and other liquids." By S. U. Pickering.

The author gives some determinations of the density of water at different temperatures which indicate sudden changes in the rate of expansion at about 10° and 18°. On examining the results obtained by Pierre, Kopp, Rosetti, Matthiessen, Solly, Despretz, and Hagen, he obtained further evidence of these changes, as well as of another change at 50—60°. Pierre's results also show marked changes at 0° and 2·5°. Pierre's results with eleven organic liquids were then examined, and in most of them there appeared to be sudden changes

at certain temperatures, which temperatures were different for different liquids. Nearly all of these results show that the densities of liquids when plotted against temperature, form a series of parabolic curves of the second order, not meeting tangentially, and differentiating, therefore, into a series of straight lines which do not meet at the points where the breaks occur.

50. "The formation of phenylindoles by isomeric change." By Walter H. Ince, Ph.D.

It has been observed by E. Fischer and Th. Schmitt (*Ber.*, 1887, 1071, 1811) that when the phenylindole $C_6H_4<\overset{C_6H_5}{\underset{NH}{C}}>CH$ is heated with zinc chloride at 170° it is converted into the isomeride $C_6H_4<\overset{CH}{\underset{NH}{}}>C\cdot C_6H_5$. The author finds that the corresponding naphthindole, $C_{10}H_6<\overset{C_6H_5}{\underset{NH}{C}}>CH$, and the methylphenylindole,

$$C_6H_4<\overset{C_6H_5}{\underset{N\cdot CH_3}{C}}>CH,$$

undergo change in a similar manner, although action takes place neither so easily nor so completely as in the simpler case.

51. "An improved Soxhlet extractor and vacuum distilling apparatus." By J. Lewkowitsch, Ph.D.

The author attaches a tap at the bottom of the syphon-tube of the Soxhlet extractor by means of which a few drops of the solvent as it runs from the extracted substance can be withdrawn to ascertain whether the extraction is complete.

For use in distilling small quantities of liquid which froth and through which it is necessary to pass an air-current while distilling under reduced pressure, he describes a flask made by inserting and sealing in just above the bulb of a Wurtz flask a tube which passes down nearly to the bottom of the flask, and there terminates in a fine point.

He also describes a simple adapter for use in fractional distillation under reduced pressure.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

History of the Royal College of Surgeons in Ireland and of the Irish Schools of Medicine; including numerous Biographical Sketches, also a Medical Bibliography, by C. A. Cameron. Dublin 1886.
From the President and Council of the College.

A Treatise on Manures, or the Philosophy of Manuring, by A. B. Griffiths. London 1889. From the Publishers.

Cosmic Evolution, being Speculations on the Origin of our Environment, by E. A. Ridsdale. London 1889.
From the Publishers.

Reports from the Laboratory of the Royal College of Physicians, Edinburgh; edited by J. B. Tuke and G. S. Woodhead. Vol. I. Edinburgh and London 1889. From the President and Council.

II. *By Purchase.*

Beiträge zur Kenntniss der Oxydations-Vorgänge in lebenden Zellen, von W. Pfeffer. Leipzig 1889.

Ueber die Affinitätsgrössen organischer Säuren und ihre Beziehungen zur Zusammensetzung und Constitution derselben, von W. Ostwald. Leipzig 1889.

Anleitung zur chemischen Analyse organischer stoffe, von G. Vortmann. I Hälfte. Leipzig und Wien 1889.

Die Schweflige Säure und ihre Verwendung bei Herstellung von Nahrungs- und Genusmitteln, von L. Pfeiffer. München 1888.

Pharmazeutische Synonyma, von C. F. Schulze. Berlin 1889.

Alcaloïdes microbiens et physiologiques (ptomaïnes et leucomaïnes), par M. de Thierry. Paris 1889.

Die Chemie des Pyridins und seiner Derivate, unter Benutzung eines Manuscriptes des A. Calm, herausgegeben von K. Buchka. Erste Lieferung. Braunschweig 1889.

At the next meeting, on June 6th, the following papers will be read:—

"Experimental researches on the Periodic Law." By Dr. B. Brauner.

"The Amylodextrin of W. Naegali." By H. T. Brown and G. H. Morris, Ph.D.

"The determination of the molecular weights of the carbohydrates." Part 2. By the same.

"Researches on silicon compounds." Part 5. By Prof. Emerson Reynolds, F.R.S.

"The isomerism of the alkyl derivatives of mixed diazoamido-compounds." By Prof. Meldola, F.R.S., and F. W. Streatfeild.

"The atomic weight of zinc." By Dr. Gladstone, F.R.S., and W. Hibbert.

"The amount of nitric acid in the rain-water at Rothamsted with notes on the analysis of rain-water." By R. Warington, F.R.S.

"The product of the action of sulphur on resin." By G. H. Morris, Ph.D.

FARADAY LECTURE.

Professor Mendeleeff's lecture will be on the Periodic Law of the Chemical Elements; it will be delivered in the theatre of the Royal Institution, Albemarle Street, W., on Tuesday, June 4th, at 8.30 P.M. Fellows requiring additional tickets for the Faraday Lecture are requested to apply to Mr. Hall. The tickets are available for ladies.

The dinner at which the Fellows will entertain Professor Mendeleeff will take place at the Holborn Restaurant on Wednesday, June 5th, at 7 P.M. Tickets may be obtained from Mr. Hall, price half-a-guinea, not including wine.

It is requested that Fellows proposing to be present at the dinner will at once notify their intention to Mr. Hall.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 70. Session 1889–90.

June 4th, 1889. Dr. W. J. Russell, F.R.S., President, in the Chair.

Professor Mendeleeff's Faraday lecture on the Periodic Law of the Chemical Elements, owing to the enforced absence of the lecturer, was read by the Secretary.

At the conclusion of the lecture, a vote of thanks to Professor Mendeleeff was moved by Professor Frankland and seconded by Sir F. A. Abel.

The Faraday medal was then presented by the President to Mr. Anderson, by whom it was received on behalf of Professor Mendeleeff.

June 6th, 1889. Dr. W. J. Russell, F.R.S., President, in the Chair.

Messrs. Alfred Edward Sibson, M. Carleton Williams, C. W. Priestley, A. L. Stern, T. E. J. Cridland and B. Brauner were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Frank Thornton Addyman, Queenwood College, Hants; Charles Frederick Baker, B.Sc., 27, London Road, N.W.; John Simpson Ford, 11, Abbotsford Park, Edinburgh; J. T. Norman, 2, Mornington Road, Regent's Park, N.W.; Sydney Steel, Fairlawn, Blackheath; John Bishop Tingle, Jäger Strasse, F/iv, Munich.

The President drew attention to the large number of interesting papers to be brought before the Society that evening, and expressed the hope that the authors present would endeavour to give an account of the essentially important points in their communications without entering into details which could not be appreciated by listeners. He was of opinion that communications made at the meetings should almost invariably be of a different character to the published papers, and should be divested of details; and he ventured to express the hope that authors generally would accept this suggestion.

The following papers were read:—

52. "Experimental researches on the Periodic Law. Part I. Tellurium." By B. Brauner, Ph. D.

The author gives a detailed account of his attempts to determine the atomic weight of tellurium by as many different methods as possible; in all 11 were adopted, but each gave a different result, varying from 125—140. He eventually succeeded, but with great difficulty, in preparing what appeared to be pure tellurium tetrabromide, and on most carefully analysing this obtained the value Te = 127·64 (O = 16). This number, however, is incompatible with the position of tellurium in the periodic system, and having satisfied himself that there were no experimental errors which could account for the discrepancy, the author was forced to conclude that what had hitherto been regarded as pure tellurium contained foreign elements. By submitting tellurium solutions to a systematic fractional precipitation, he has, in fact, succeeded in obtaining a variety of substances, some of which are undoubtedly novel elements. One of these it is proposed to call *Austriacum* (*Austrium*). In all probability this is the *Dvi-tellurium* (212), the probable existence of which was pointed out for the first time by Mendeleeff in his recent Faraday lecture. From analyses made with material the uniformity of which is not yet quite established, the author is satisfied that the atomic weight of the element in question approaches very closely to that indicated by Mendeleeff. In addition, there is at least one other novel constituent, and this appears to be more or less closely allied to arsenic and antimony. It follows that true tellurium has yet to be discovered, and that its atomic weight and properties remain to be determined.

Discussion.

Mr. J. Newlands remarked that he had always placed tellurium below iodine; he had no doubt that the exceptional atomic weight would ultimately be rectified, and that true tellurium, when isolated, would be found to have an atomic weight near 125.

53. "The amylodextrin of W. Nägeli and its relation to soluble starch." By Horace T. Brown and G. Harris Morris, Ph.D.

Amylodextrin, described by W. Nägeli in 1874, is prepared by the long-continued action of cold dilute acids on intact starch-granules; when purified by dissolution in water and precipitation with alcohol, it forms crystalline spherules, closely resembling the well-known spherules of inulin. Amylodextrin is coloured a reddish-brown by iodine. The values obtained on analysis of the purified substance were—

$[\alpha]_j$ ..	3·86	206·25°	κ	3·86	9·07°

which correspond to a percentage composition of—

Maltose	14·87	which requires	$[\alpha]_j$ ..	3·86	205·4°
Dextrin	85·13		κ	3·86	9·07
	100·00				

The substance is shown to be a definite compound: (*a*) by its absolute unfermentability by ordinary top fermentation yeast; (*b*) by the impossibility of differentiating it by fractional precipitation or partial dissolution; (*c*) by its passing through a dialyser in an unaltered form; and (*d*) by its distinct crystalline form.

The authors consider amylodextrin to be analogous in composition to the malto-dextrin previously described by them (Trans., **47**, 528), and assign to it the formula $C_{12}H_{22}O_{11}\cdot(C_{12}H_{20}O_{10})_6$; *i.e.*, it may be regarded as constituted of one *amylon* or maltose group in combination with six *amylin* or dextrin groups.

A determination of the molecular weight by Raoult's method gave the following numbers:—

	Calculated for $C_{12}H_{22}O_{11}\cdot(C_{12}H_{20}O_{10})_6$.	Found (mean).
A	0·0096	0·0086
M	1962·0	2220·0

Amylodextrin, like malto-dextrin, is rapidly and completely converted into *maltose* by the action of diastase.

The authors point out that amylodextrin has been confused by former workers with soluble starch, on the one hand, and with the so-called starch-cellulose, on the other hand. From these substances it is differentiated by its solubility, its iodine coloration, and its behaviour with diastase and with acids. When acted on by diastase, soluble starch yields a mixture of maltose and dextrin, corresponding to the No. 8 equation of the authors' previous papers, whilst amylodextrin

is completely converted into maltose by the same treatment. The authors also show that soluble starch is the first product of the action of cold dilute acids on starch, and that this is slowly hydrolysed to amylodextrin, a portion of the starch substance at the same time going into solution as dextrose.

54. "The determination of the molecular weights of the carbohydrates. Part II." By Horace T. Brown and G. Harris Morris, Ph.D.

After referring to their former paper on this subject (Trans., 1888, 610), and stating that the results there given have been since confirmed by Tollens and Mayer (*Ber.*, 1888, 1566 and 3508), and by de Vries (*Compt. rend.*, **106**, 751), the authors give the results of the determination by Raoult's method of the molecular weights of the following carbohydrates:—

Galactose.

	Calculated for $C_6H_{12}O_6$.	Found (mean).
A	0·106	0·1073
M	180·0	177·0

Inulin.

	Calculated for $2(C_{36}H_{62}O_{31})$.	Found (mean).
A	0·0096	0·0087
M	1980·0	2176·0

Kiliani has assigned the formula $C_{36}H_{62}O_{31}$ to inulin, but the authors' results point to the correct value being double this. They have already shown the great similarity between amylodextrin and inulin as regards their physical properties (see preceding Abstract), and they are inclined to regard the two substances as closely analogous in composition, thus:—

$\left\{\begin{matrix}(C_{12}H_{22}O_{11})_2\\(C_{12}H_{20}O_{10})_4\end{matrix}\right.$; Inulin; M = 1980.

$\left\{\begin{matrix}C_{12}H_{22}O_{11}\\(C_{12}H_{20}O_{10})_6\end{matrix}\right.$; Amylodextrin; M = 2286.

although the amylin and amylon groups in each possess very different optical and other properties, and the products of hydrolysis with dilute acid are very different.

Malto-dextrin.

	Calculated for $\left\{\begin{matrix}C_{12}H_{22}O_{11}\\(C_{12}H_{20}O_{10})_2\end{matrix}\right.$.	Found (mean).
A	0·0191	0·0197
M	990·0	965·0

Starch.—It was found impossible to apply Raoult's method to starch-paste; solutions of soluble starch produced so slight a depression that no reliable results could be obtained: a number of fairly concordant results, however, pointed to a molecular weight of 20,000 to 30,000. In order to ascertain whether the failure in this case was due to a high molecular weight, and not to the fact that the method was inapplicable to colloid substances, an arabinic acid, having a rotatory power $[\alpha]_j = +61{\cdot}16°$, was examined; this gave A = 0·0265, M = 717·0, thus rendering it probable that the small influence exercised by soluble starch was due to its high molecular weight.

Indirect evidence was then sought for by an examination of the dextrins. The authors have previously shown that when starch is broken down by diastase, a resting stage in the reaction is reached when the amount of dextrin produced corresponds to *one-fifth* by weight of the starch taken, and that *the molecule of this stable dextrin is one-fifth of the size of the starch-molecule from which it has been derived.* Determinations made with several specimens of this low dextrin gave the following mean values:—

	Mean values.	Calculated for $20C_{12}H_{20}O_{10}$.
A	0·0030	0·0029
M	6221·0	6480·0

and consequently the formula of soluble starch would be $5(C_{12}H_{20}O_{10})_{20}$, and its molecular weight 32,400. The endeavour was also made to apply Raoult's method to the determination of the question whether the dextrins are a series of polymers or whether they are simply metameric. For this purpose a number of the higher dextrins were prepared from starch-transformations which had been stopped at an early stage of hydrolysis. All the numbers obtained show that the freezing method affords no evidence of there being any difference in molecular weight between the high and low dextrins, the numbers being, in fact, almost identical.

From a consideration of the results obtained with soluble starch, and with dextrins of varying position in the series, the authors conclude that the evidence points to the conclusion that the dextrins are metameric and not polymeric compounds. They therefore abandon their former working hypothesis of the hydrolysis of starch, and now suppose the starch-molecule to consist of four complex amylin-groups, arranged round a fifth similar group, constituting a molecular nucleus. When hydrolysis takes place this complex is broken up, four amylin-groups being liberated, which in turn are capable of undergoing complete hydrolysis into malto-dextrins, and ultimately into maltose, whilst the fifth amylin group which constituted the

nucleus of the original molecule resists the action of hydrolysing agents and forms the stable dextrin of the No. 8 equation.

Each amylin group of the five has the formula $(C_{12}H_{20}O_{10})_{20}$, corresponding to a molecular weight of 6480; the molecule of soluble starch being represented by $5(C_{12}H_{20}O_{10})_{20}$, corresponding to a molecular weight of 32,400.

Discussion.

Dr. Gladstone remarked that the observations made by Mr. Hibbert and himself on the molecular weights of colloid substances completely confirmed those now brought forward by the authors. He believed Raoult's method to be capable of distinguishing polymers, as satisfactory results had been obtained on examining polymeric C_5H_8 compounds.

Dr. Armstrong remarked that as both the universal applicability of Raoult's method and the molecular weights of colloids were in question, neither was at present a safe standard. He was not satisfied with the conclusion arrived at in the case of the dextrins.

55. "Researches on silicon compounds. Part V." By J. Emerson Reynolds.

The author has already shown that silicon tetrabromide unites with some amidic compounds, especially thiocarbamide, allyl-, phenyl-, and diphenyl-thiocarbamides, without loss of halogen, and produces compounds of the type $(CSN_2H_4)_8SiBr_4$. In this part a detailed account is given of the products of interaction of silicon haloids with excess of aniline, orthotoluidine and paratoluidine, and the three following bodies are described which result from the complete substitution of halogen by NHR-groups derived from the amido-compounds.

Silicotetraphenylamide, $Si(NHC_6H_5)_4$, a beautiful crystalline body, is obtained from its carbon disulphide solution in fine, monoclinic forms which have been subjected to a determined crystallographic examination by Professor Sollas.

Silicoparatolylamide, $Si(pNHC_7H_7)_4$, is obtained from its benzene solution in botryoidal masses of fine needles; it is but slightly soluble in ligroin, and therefore is precipitated by it from a benzene solution.

Silico-orthotolylamide, $Si(oNHC_7H_7)_4$. This differs from the para-compound in being soluble in ligroin. When the mixed benzene and ligroin solution is distilled a very thick, syrupy liquid remains which, after long exposure in a vacuum, gradually affords a quantity of minute needles which do not exhibit any tendency to form aggregations.

56. "The isomerism of the alkyl-derivatives of mixed diazoamido-compounds." By R. Meldola, F.R.S., and F. W. Streatfeild.

The authors first describe a detailed series of experiments under-

taken with the object of testing the chemical individuality of the mixed diazoamide $(p)NO_2{\cdot}C_6H_4{\cdot}N_3H{\cdot}C_6H_4{\cdot}NO_2(m)$, and its alkyl-derivatives. A critical study of the compound has served to confirm the former result that this compound and its alkyl-derivatives are perfectly definite, and that they cannot be formed by crystallising together the corresponding symmetrical compounds. Mixtures of $(p)NO_2{\cdot}C_6H_4{\cdot}N_3H{\cdot}C_6H_4{\cdot}NO_2(p)$ and $(m)NO_2{\cdot}C_6H_4{\cdot}N_3H{\cdot}C_6H_4{\cdot}NO_2(m)$ can be easily separated into their constituents by crystallisation from alcohol. The same holds good for the corresponding ethyl-derivatives, which are equally capable of being separated whether formed separately and afterwards mixed or whether a mixture of the unalkylated compounds is first prepared and then afterwards ethylated by the authors' method. A more extended study of the mixed diazoamides containing a halogenised radicle has served to convince the authors that the mixed diazoamides are most difficult to prepare in a state of purity, owing to the tendency to the formation of the corresponding normal (symmetrical) compounds at the same time. It is pointed out as a result of this experience that all the mixed diazoamides prepared by Continental investigators have been of very doubtful purity, and that in nearly all cases a nitrogen determination only has been considered sufficient to establish the composition. It is shown that the presence of one or the other of the normal compounds might thus escape detection, as a considerable percentage of such an impurity would not affect the percentage of nitrogen beyond the ordinary limits of experimental error. Criticising their own former work in the light of this experience, the authors have come to the conclusion that the diazoamides from para- and meta-nitraniline are not so well adapted for ascertaining when a pure product is obtained as those mixed compounds which form the subject of the present paper, and which contain a halogenised radicle on one side of the N_3H-group. The mixed compound derived from the two nitranilines might obviously contain some of the dipara- or dimeta-compound without affecting the analytical numbers, since both sides of the N_3H-group have the same composition. Many new preparations have, therefore, been made and studied, and the melting points revised with the following results :—

$(p)NO_2{\cdot}C_6H_4{\cdot}N_3H{\cdot}C_6H_4{\cdot}NO_2(m)$ ...	212—213° (instead of 211).
$(p)NO_2{\cdot}C_6H_4{\cdot}N_3(C_2H_5){\cdot}C_6H_4{\cdot}NO_2(m)$	151—155° (instead of 148).

This vagueness of melting point has been found to be a very general character of all the alkyl-derivatives of mixed diazo-amides prepared by direct alkylation, and is attributed to the circumstance that the melting point is also the point of decomposition, this instability being especially observable in the case of the compounds containing

strongly acid radicles. The authors restate their original proposition, viz., that every pair of amines, $X{\cdot}NH_2$ and $Y{\cdot}NH_2$, can give rise to *three* isomeric alkyl-derivatives:—

1. By the action of diazotised $X{\cdot}NH_2$ on $Y{\cdot}NHR'$.
2. By the action of diazotised $Y{\cdot}NH_2$ on $X{\cdot}NHR'$.
3. By the direct alkylation of $X{\cdot}N_3H{\cdot}Y$.

A large number of triplets have been prepared, all of which conform to this proposition. Their formulæ and melting points are:—

I.	$(p)NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}N(CH_3){\cdot}C_6H_4{\cdot}Br(p)$	151—151·5°
	$(p)Br{\cdot}C_6H_4{\cdot}N_2{\cdot}N(CH_3){\cdot}C_6H_4{\cdot}NO_2(p)$.....	163—164
	$(p)NO_2{\cdot}C_6H_4{\cdot}N_3(CH_3){\cdot}C_6H_4{\cdot}Br(p)$	150·5—151·5°
II.	$(p)NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}N(C_2H_5){\cdot}C_6H_4{\cdot}Br(p)$.....	139—140
	$(p)Br{\cdot}C_6H_4{\cdot}N_2{\cdot}N(C_2H_5){\cdot}C_6H_4{\cdot}NO_2(p)$	124—125
	$(p)NO_2{\cdot}C_6H_4{\cdot}N_3(C_2H_5){\cdot}C_6H_4{\cdot}Br(p)$.....	115—116
III.	$(m)NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}N(CH_3){\cdot}C_6H_4{\cdot}Br(p)$.....	144°
	$(p)Br{\cdot}C_6H_4{\cdot}N_2{\cdot}N(CH_3){\cdot}C_6H_4{\cdot}NO_2(m)$.....	160·5—161°
	$(p)Br{\cdot}C_6H_4{\cdot}N_3(CH_3){\cdot}C_6H_4{\cdot}NO_2(m)$	125—137·5 (much decomposition).
IV.	$(m)NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}N(C_2H_5){\cdot}C_6H_4{\cdot}Br(p)$	111°
	$(p)Br{\cdot}C_6H_4{\cdot}N_2{\cdot}N(C_2H_5){\cdot}C_6H_4{\cdot}NO_2(m)$.....	135—136°
	$(p)Br{\cdot}C_6H_4{\cdot}N_3(C_2H_5){\cdot}C_6H_4{\cdot}NO_2(m)$	96—117 (much decomposition).
V.	$(p)Br{\cdot}C_6H_4{\cdot}N_2{\cdot}N(CH_3){\cdot}C_6H_4{\cdot}CH_3(p)$.....	113—114°
	$(p)CH_3{\cdot}C_6H_4{\cdot}N_2{\cdot}N(CH_3){\cdot}C_6H_4{\cdot}Br(p)$.....	99—99·5
	$(p)CH_3{\cdot}C_6H_4{\cdot}N_3(CH_3){\cdot}C_6H_4{\cdot}Br(p)$	97—97·5
VI.	$(p)Cl{\cdot}C_6H_4{\cdot}N_2{\cdot}N(CH_3){\cdot}C_6H_4{\cdot}CH_3(p)$.....	99·5—100°
	$(p)CH_3{\cdot}C_6H_4{\cdot}N_2{\cdot}N(CH_3){\cdot}C_6H_4{\cdot}Cl(p)$	91—92
	$(p)CH_3{\cdot}C_6H_4{\cdot}N_3(CH_3){\cdot}C_6H_4{\cdot}Cl(p)$	80—82

The isomerism of these triplets is shown not only by their melting points, but also by their products of decomposition by cold hydrochloric acid. These products have in all cases been examined quantitatively, and the general results are shown by the equations—

1. $X{\cdot}N_2{\cdot}NR'{\cdot}Y + HCl = X{\cdot}N_2{\cdot}Cl + Y{\cdot}NHR'$.
2. $Y{\cdot}N_2{\cdot}NR'{\cdot}X + HCl = Y{\cdot}N_2{\cdot}Cl + X{\cdot}NHR'$.
3. $2X{\cdot}N_3R'{\cdot}Y + 2HCl = X{\cdot}N_2{\cdot}Cl + Y{\cdot}N_2{\cdot}Cl + X{\cdot}NHR' + Y{\cdot}NH{\cdot}R'$.

From this it appears that the alkyl-derivatives of the mixed diazoamides always split up like the unalkylated products into a mixture of the two diazochlorides and two alkylamines. The most feasible interpretation of these facts is that the *mixed* diazoamides have double

the molecular weight usually assigned to them, and in support of this conclusion the authors have discovered that the mixed alkyl-diazoamides can be synthesised by simply boiling the alcoholic solutions of the other two isomerides of the triplet, thus :—

$$X{\cdot}N_2{\cdot}NR'{\cdot}Y + Y{\cdot}N_2{\cdot}NR'{\cdot}X = (X{\cdot}N_3R'{\cdot}Y)_2.$$

This observation must necessarily lead to a considerable modification in the existing views respecting the constitution of the diazoamides generally, and experiments in the direction indicated are being carried on both by means of Raoult's method of determining molecular weights as well as by purely chemical methods.

57. "The atomic weight of zinc." By J. H. Gladstone, Ph.D., F.R.S., and Walter Hibbert.

The authors have observed that when amalgamated zinc is used as anode in a zinc sulphate voltameter, the metal dissolved appears to be free from impurity. This they attribute to the electrochemical relations between zinc and its ordinary impurities, the latter being less readily attacked than the more electropositive metal. Results obtained in different voltameters with the same current showed a very close agreement, and the authors therefore determined the atomic weight of zinc by applying Faraday's law of electrolysis.

For this purpose a series of copper, silver and zinc voltameters were arranged in a simple circuit, and the quantity of zinc dissolved was compared with the weights of deposited silver and copper.

The results of five experiments are given, but as two zinc voltameters were employed in each, the data afford 10 comparisons of the equivalents of silver and zinc, and eight comparisons of those of zinc and copper. The mean ratio of the equivalents of silver and zinc is 3·298 $\pm$ 0·00008. Taking the atomic weight of silver as 107·93, this ratio gives 65·44 as the atomic weight of zinc. If silver is taken as 107·66, zinc = 65·29.

The copper sulphate voltameter is not so accurate as the silver one, owing to the solvent action of the solution on copper. But by keeping the density of the current within certain limits, this action can be made extremely small. Still the ratio Zn : Cu given by the experiments (1·0322) is probably rather higher than it ought to be. There is also uncertainty as to the atomic weight of copper, but the authors have used W. N. Shaw's value, 63·33. This gives 63·33 × 1·0322 = 65·37 as the atomic weight of zinc.

The two comparisons indicate 65·3 as being very near the true value. This is higher than the results obtained in recent years by Marignac, Baubigny, Morse and Burton, but lower than that given by Reynolds and Ramsay.

58. "The amount of nitric acid in the rain-water at Rothamsted, with notes on the analysis of rain-water." By R. Warington, F.R.S.

Determinations of chlorine and sulphuric acid have been made in the Rothamsted rain-water for several years, and new determinations of ammonia for five years (Trans., 1887, 501); new determinations of nitric acid are now communicated.

The first method employed involved the concentration of 10 lbs. of rain-water with a little magnesia, filtering, and determining the nitric acid as nitric oxide gas by Schloesing's method. This plan gave low results with the stronger rain-waters; the loss apparently took place during the last stage of the concentration, being due to a reduction of a portion of the nitrates by the agency of the organic matter and lead which the water contained.

The method finally adopted involves the reduction of the nitric acid to ammonia by means of the copper-zinc couple. 1 litre of the water is boiled in a retort with magnesia till 250 c.c. have distilled; in the distillate the ammonia present in the water is determined; the residue is diluted to 800 c.c., copper-zinc couple added, and the whole allowed to stand three days at 20—24°; the ammonia present is then determined by distillation and Nesslerising, and its equivalent in nitric acid calculated.

The rain of 20 months, analysed by the copper-zinc method, contained an average of 0·138 of nitrogen as nitric acid per million of water; this is a little higher than that found by Way in 1855-56, namely, 0·12 per million, but is almost identical with that found by Frankland as a mean of his analyses of Rothamsted rain in 1869–70. In a whole year, 1888–89, with a rainfall of 29·27 inches, the quantity of nitric nitrogen in the rain was 0·917 lb. per acre, and the nitrogen as ammonia 2·823 lbs., or a total of 3·74 lbs. These quantities are compared with those found by other experimenters.

A brief account of the methods employed at Rothamsted in determining the ammonia, chlorine and sulphuric acid in rain is then given.

59. "The product of the action of sulphur on resin." By G. Harris Morris, Ph.D.

Pelletier and Walter, in 1838, described a solid hydrocarbon which they separated from the products of the distillation of resin; later observers obtained a similar product by distilling resin with sulphur. The author has examined this latter substance.

The hydrocarbon separates from its solutions in alcohol, benzene, &c., in pale yellow crystalline scales, which melt at 84—85° C.; it

boils without decomposition slightly above the boiling point of mercury. Its composition is expressed by the formula $(C_5H_6)_n$; the density determined by Victor Meyer's method, using the vapour of sulphur, was 160·07, whilst $(C_5H_6)_5$ requires 165.

From the examination of a number of its derivatives the author concludes that Kelbe is wrong in regarding the substance obtained by the action of sulphur on resin as identical with retene.

60. "The vapour-pressures and specific volumes of similar compounds of elements in relation to the position of those elements in the periodic system." Part I. By Sydney Young, D.Sc.

Determinations have been made of the vapour-pressures and specific volumes of the four haloid derivatives of benzene and also of benzene itself, within very wide limits of temperature; benzene, fluobenzene and chlorobenzene having been heated to their critical points, 288·5°, 286·55° and 360·8° respectively.

It is shown that if the four haloid derivatives are compared at such temperatures that their vapour-pressures are equal, the (absolute) temperatures and also the specific volumes bear a constant ratio to each other, whatever the common pressure.

But on comparing benzene with one of its haloid-derivatives it is found that these simple relations do not hold. The ratios of the absolute temperatures of benzene and fluobenzene corresponding to equal pressures are very exactly expressed by the equation $R' = R + ct$, where R′ is the ratio at a pressure for which the corresponding centigrade temperature of fluobenzene is t, $R = 0{\cdot}0838$, and $c = 0{\cdot}0000313$.

If the specific volumes of benzene and fluobenzene are compared at temperatures corresponding to pressures which are in all cases proportional to the critical pressures of the two liquids, the ratios of the volumes are found to be very nearly constant. If, again, the specific volumes are compared at absolute temperatures which are in all cases proportional to the absolute critical temperatures, the ratios of the volumes are again nearly constant. But the two methods of comparison are not equivalent—though that is stated to be the case by Van der Waals—and they cannot both be correct, for it cannot be taken as even approximately true that the absolute temperatures corresponding to pressures which are always proportional to the critical pressures are themselves proportional to the absolute critical temperatures. Moreover, the values obtained by the two methods of comparison are not quite the same, and for two liquids which are chemically dissimilar, the values may differ considerably. It is impossible at present to say with certainty which method of comparison

gives the better results, but the author is inclined to think that the comparison at "proportional" or "corresponding" pressures is most likely to be correct.

The relations of Van der Waals as regards "corresponding" temperatures, pressures and specific volumes of liquid hold good accurately in the case of the haloid derivatives of benzene, but the critical pressures of the haloid derivatives are *equal* and the comparisons must therefore be made at *equal* pressures.

Fluorine, chlorine, bromine and iodine belong to the same group in the periodic table; the effect of substituting one of these elements for another in the compounds of the type C_6H_5R, as regards the relations between vapour-pressure, temperature and specific volume is extremely simple, but if hydrogen be substituted for one of the halogens, the changes produced are much greater.

61. "The vapour-pressures of quinoline." By Sydney Young, D.Sc.

Four years ago Dr. Ramsay and the author, in describing their method of obtaining constant temperatures (*Trans. Chem. Soc.*, 1885, 640, and 1886, 37), gave tables of the vapour pressures of various pure liquids from 0° to 360° C. One of these, methyl salicylate, gives less satisfactory results than the others, and it is proposed to substitute quinoline for it. Determinations of the vapour-pressures of quinoline are described, and a table is given for each degree between 180° and 240°.

At the next meeting, on June 20th, there will be a ballot for the election of Fellows, and the following papers will be read:—

"The nature of solutions as elucidated by a study of their freezing temperatures." By S. U. Pickering.

"Propionate and butyrate of phenyl and propionyl- and butyrl-phenol." By Dr. Perkin, F.R.S.

"Observations on the melting points of methylated and ethylated salicylic and anisic aldehydes." By the same.

"Note on the oxidation of paradiamines." By Prof. Meldola and R. E. Evans.

"Monobenzyl-derivatives of the phenylenediamines." By Prof. Meldola and J. H. Coste.

"Note on a yellow pigment in butterflies." By F. G. Hopkins.

"Zinc dextrosate." By A. C. Chapman.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 71. Session 1889–90.

June 20th, 1889. Dr. W. J. Russell, F.R.S., President, in the Chair.

Messrs. James Hall, B.A., B.Sc., and J. W. Slater were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Thomas William Dukes, Cape Town, South Africa; Theodore Francis Garrett, 36, Drakefell Road, St. Catherine's Park, Hatcham, S.E.; Eric Henry Jackson, B.Sc., Harefield, Morley Road, Southport; William Whitehouse, Myrtle Villa, Dixon's Green, Dudley.

The following were elected Fellows of the Society:—Edward Wightman Bell; William D. Cargill, B.Sc.; George William Howard; Frederick Charles Knight; Henry W. Morrow, B.S.; D. O'Mahoney; Benjamin Phillips; Robert Redwood; Emanuel Roberts; Robert M. W. Swan.

The following papers were read:—

62. "Observations on the melting point of some salicylic and anisic compounds." By W. H. Perkin, Ph.D., F.R.S.

The author, after referring to his paper published in the Journal of the Society in 1867, in which methylated and ethylated salicyl aldehydes are described as nearly colourless fluids which do not solidify when cooled in a freezing mixture, and to the apparently contradictory results of Voswinckel (*Ber.*, 1882, 2024)—who states that methylated salicyl aldehyde is a solid melting at 35°—points out the

curious fact that, although this latter aldehyde does not easily crystallise in a freezing mixture, it can be made to do so; the crystals, however, melt at about 2·7—3°. On evaporating an ethereal solution of the aldehyde, he obtained prismatic crystals, having the melting point given by Voswinckel, and it was found that if the oily aldehyde be touched with one of these it immediately becomes a solid mass having a melting point of 35°. On re-melting this solid and then cooling in a freezing mixture, crystals melting at 2·7—3° can again be obtained. It is therefore established that methylated salicyl aldehyde forms crystals of two kinds, having melting points differing by about 32°.

Ethylated salicyl aldehyde can also be made to crystallise; the crystals melt at about 6° or 7°.

Anisic aldehyde also crystallises when cooled; although a para-compound, it melts at a lower temperature than either modification of methyl salicyl aldehyde, viz., at 0·02°.

Ethylic anisate easily crystallises (m. p. = 7°), but ethylic methylsalicylate has not as yet been obtained in a crystalline condition.

63. "The action of propionyl and butyryl chloride on phenol." By W. H. Perkin, Ph.D., F.R.S.

In preparing phenyl propionate and butyrate by means of phenol and propionyl and butyryl chloride, the author has observed that secondary products are also formed, which are proved to be new phenols containing acid radicles in place of hydrogen in the phenyl-group, viz., $C_3H_5O\cdot C_6H_4\cdot OH$, and $C_4H_7O\cdot C_6H_4\cdot OH$. They are both crystalline compounds, propionylphenol melting at 148·5°, butyrylphenol at 91°; they are soluble in ammonia solution.

Phenylic acetate, which has been previously described as an oil, was obtained in a crystallised condition; it melts at 20° and boils at 211° (corr.).

Phenylic butyrate, which has not been previously prepared, is an oil boiling at 227—228° (corr.).

64. "The nature of solutions as elucidated by a study of their freezing temperatures." By S. U. Pickering.

A series of determinations of the freezing temperatures of mixtures of sulphuric acid and water was undertaken in order to obtain further confirmation of the existence in solution of the various hydrates which had been indicated by the densities, heat of dissolution, heat capacity and electric conductivity of these solutions, as well as to throw some light on Raoult's method of determining molecular weights.

The determinations with solutions containing over 4 per cent. H_2SO_4 were attended with considerable difficulty, as the solution does not freeze, but one of its constituents crystallises out, the change being identical in nature with the crystallisation of a salt from a saturated solution; what has to be determined, therefore, is the temperature at which the given solution becomes saturated. This was done by cooling the liquid down till a good crop of crystals was obtained; it was then put in a vessel of water, and the rise of temperature noted at every half minute; the temperature at which the last crystals had disappeared was signalised by a sudden alteration in the rate of this rise.

The author has, so far, plotted the results only against percentage composition. The general results are represented by three independent curves, in which water, $H_2SO_4 \cdot H_2O$, and H_2SO_4 itself are the substances which crystallise out.

The first of these curves is represented by an approximately straight line as far as 8 or 9 per cent. H_2SO_4, falling at the rate of about 0·5° for every 1 per cent.; it then curves rapidly downwards, the crystallising temperature of a 30 per cent. solution being 36°; a little beyond this point it appears to become almost vertical. From 30 to 77 per cent. no freezing points have been attained. At this latter strength the crystallisation of the monohydrate begins. This crystallisation is represented by a curve with two branches, having its highest point at 84·5 per cent. (the composition of $H_2SO_4 \cdot H_2O$) and 8·5°, and falling away from this point on either side, at first gradually, and then abruptly. At about 94 per cent. this curve meets that representing the crystallisation of H_2SO_4, the temperature being −31°; the H_2SO_4 curve rises from this point in an approximately straight line up to 100 per cent. and 10·35°, when it turns abruptly down again in a curvilinear direction, the determinations having been extended as far as 101 per cent.

A closer inspection of these several curves shows that none of them are continuous, but that they are made up of separate curves or straight lines, which seem to be quite independent of each other, and show breaks of a most marked character, often corresponding to differences five or ten times greater than the experimental error. These breaks occur in every case at the same points as those observed by the author in the densities and other properties, and are of a very much more certain character than in any of the other cases. Of the 17 hydrates of sulphuric acid which he previously indicated, 12 are very satisfactorily confirmed by the present observations; the other five (H_2SO_4 with 2, 4, 5, 9 and 13 H_2O) would be shown only in that portion of the diagram where no freezing points have yet been reached. In addition to this, there appears to be three other breaks,

which the previous work would have been insufficient to show, at 98·7, 86, and 82·5 per cent., corresponding to $12H_2SO_4 \cdot H_2O$, $7(H_2SO_4 \cdot H_2O) \cdot H_2SO_4$, and $7(H_2SO_4 \cdot H_2O) \cdot H_2O$, as well as a break at 100·7 per cent., representing $27H_2SO_4 \cdot SO_3$, and at 100 per cent., or H_2SO_4 itself. It is especially noteworthy that the breaks at the extreme end of the curve corresponding to H_2SO_4 with 500, 1400 and 5000 H_2O have been fully confirmed.

The marked character of these breaks (which are apparent without any differentiation) leads to the hope that the method may be applicable in the case of solutions of organic liquids where other methods would fail.

Each of the three main curves which represent the general results tend downwards at an increasing rate as we pass from the highest points in them, and this tendency would also be exhibited if the results were plotted against molecular instead of percentage composition. This, the author shows, is what their character should be if hydrates were formed in solution, whereas on the physical theory of solution, they should tend downwards at a diminishing rate; so that the general form of the curves, independent of there being breaks in them, is conclusive in favour of the hydrate theory.

Passing on to the bearing of these results on Raoult's method, the author repeats his assertion that, at the best, this method could only give us the molecular weights of substances in the gaseous condition at the temperature of the determination, for in dilute solutions the molecules of the dissolved substance are as far removed from each other as they are when vaporised.

There are, however, no theoretical considerations which justify our regarding the molecular weight thus obtained in the same light as that obtained from vapour-densities. The vapour-density is a constant within experimental error throughout a very long range of conditions, whereas the lowering of the freezing point could only be a constant on the supposition that dissolution is entirely physical and that the dissolved molecules act independently of the solvent. The present results show that it is not a constant, and that we have no grounds for supposing it to be such even with extremely dilute solutions. The irregularities and breaks which characterise the whole results have been traced back as far as a 0·1 per cent. solution, and a further extension of the determinations, if possible, would simply reveal a continuation of these irregularities. On the other hand, it must be admitted, as, indeed, the practical results prove, that these irregularities would often lead to no great error in the molecular weight found, provided the solutions used are not too strong.

The author shows that such would be the case with the sulphuric acid curves, when the crystallisation of water is used to determine

the molecular weight of H_2SO_4, or that of sulphuric acid to determine the molecular weight of H_2O. But the case is otherwise when we use the crystallisation of the monohydrate to determine the molecular weight of H_2SO_4 on the one hand and H_2O on the other. Within 5 per cent. of $H_2SO_4{\cdot}H_2O$ we should get results such as 18 for H_2SO_4 and 6 for H_2O. This shows that, although Raoult's method may give approximately correct results in many cases, we can never rely on it without performing an extensive series of experiments. There are no theoretical considerations which would lead us to suppose that it is reliable, and this investigation proves that each case has peculiarities of its own, which may lead to an entirely erroneous molecular weight.

65. "Note on the determination of the molecular weight of substances in solution especially colloids." By Henry E. Armstrong.

The fundamental conception underlying the now very general acceptation of the Raoult methods of determining molecular weight is undoubtedly the conception introduced by Van't Hoff that substances are present in dilute solutions in a state comparable with the gaseous state (cf. Ramsay, *these Proceedings*, 1889, p. 44). But in gases, even in the most imperfect, the individual molecules exercise a very slight mutual attractive influence; otherwise, in fact, the gaseous state could not subsist. When liquefaction ensues, it would appear to be owing to, and to involve the exertion of, such mutual intermolecular attractions; and however continuous the states of gas and liquid may appear from a mathematical standpoint, the continuity would seem to be only that kind of continuity which is observed in dissociative changes generally. Although statistical analysis may support the conclusion that the gaseous state and that which obtains in a dilute solution are comparable, a consideration of the phenomena in the light of our knowledge of intermolecular relationships cannot at present be held to justify any such assumption; how can it be permissible, in fact, to compare the approximate truth of the laws of Boyle and Gay-Lussac with Raoult's, if in solution an all-important part be played by a factor—the solvent—which, in the case of gases, may be left almost entirely out of consideration; and if water be not a neutral substance and the phenomena of dissolution are, as many believe, of a high order of complexity.

The regular and rational results which are obtained on applying the Raoult methods to dilute solutions of substances of known molecular weight are undoubtedly very striking and likely to carry conviction to many minds that the methods are of universal application; but other equally striking coincidences have been observed.

Thus it is highly remarkable that the hydroxides generally—in dilute solutions be it observed—have the same heat of neutralisation. This illustration is of special moment, for if we consider the supposed interagents alone and disregard the solvent as a chemical agent, it is inconceivable that such should be the case; the result must be in some way a consequence of a higher law not yet clearly perceptible through the haze of complexity which so enshrouds the phenomena of chemical change in solution. It cannot be doubted that the constancy is conditioned by the presence of water in large relative quantity, as most irregular and dissimilar results are obtained if the comparison be made for any other than dilute solutions, just as in the case of the Raoult freezing method (cf. Beckmann, *Zeit. phys. Chem.*, 1888, 638 and 715).

If the argument here advanced be admitted, it follows that not only the molecular weight of a substance but also its *specific effect* must be taken into account; and this is undoubtedly the case. It is well known that acids and metallic salts, and indeed electrolytes generally, give abnormal results; they produce too great an effect. Arrhenius has suggested that such compounds are present in solution in a more or less dissociated condition—dissociated into their "*ions;*" that, in fact, such solutions contain a greater number of active molecules than are usually supposed to be present. Allowing for this increase in a manner which he has pointed out, "normal" results are obtained in place of the impossibly low molecular weights which result from the direct reduction of the experimental values. But if we are to accept this view, we must admit that water is a neutral substance, and that it plays no active part in electrolysis; in other words, such a conclusion directly involves the acceptation of a particular hypothesis as to the nature of electrolysis. The arguments on which this hypothesis is based, however, are mostly cases of circular reasoning, and there are many facts which apparently cannot be satisfactorily accounted for by it (cf. *B.A. Report*, 1888, 356). The one argument in favour of the dissociation hypothesis which is generally regarded as all-sufficient—the argument originally advanced by Clausius, that any E.M.F., however small it may be, produces sensible electrolysis, is one of which it would be premature to accept any explanation as final in our entire ignorance of the inner mechanism of electrical actions—while the electric current is an unsolved mystery, as was happily observed by Professor Rowland in a recent lecture—especially as there are electricians who are of opinion that the Clausius hypothesis is not necessarily the only possible solution, although at present unable to suggest a more satisfactory one. But not only is the explanation of electrolysis which is usually given of a purely "mechanical" nature, and incompatible, therefore, with the view that the

solvent plays an active part; it is open also to the objection that in framing it attention has been paid too exclusively to a certain limited number of phenomena, and that the bearing of the facts of chemistry generally as these present themselves to the mind of the chemist has been insufficiently considered. It is probable that this will soon cease to be the case, as signs are not wanting that it will ere long be recognised that chemical changes are essentially electrolytic phenomena, and that we may expect to witness the rehabilitation of Faraday's view of 1834 of "the identity of the force constituting the voltaic current or electrolytic agent with that which holds the elements of electrolytes together, or in other words with chemical affinity."

Although it may be urged that the method which Arrhenius has introduced of correcting the results obtained in the case of electrolytes is based on an incorrect interpretation of the phenomena, it does not follow that his method is necessarily a faulty one: on the contrary. Practically the method involves nothing more than the recognition of the fact that it is possible to determine with a close approach to accuracy, and to allow for, the *specific effect* which a compound exercises. This would seem to be the case. Thus Ostwald's experiments show that in the case of acids, for example, in seeking to determine the order of activity in which these may be arranged, practically the same result is arrived at, the order deduced being very similar, when very diverse properties are made the subject of study. Molecular weight does not come into evidence as a determining cause of position in such a series, compounds such as hydrogen chloride, bromide and iodide occurring together and almost at the head of the scale of activity, while hydrogen fluoride is found low down in the series. The compounds in such a series afford "abnormal" values when examined by the Raoult methods in dilute solutions owing to their exercising a greater effect than is produced by compounds which give "normal" values; the extent to which the effect produced is in excess depends on the position in the series, and if proper allowance be made on this assumption a "normal" value is necessarily obtained, *i.e.*, a value consonant with the view which on general grounds we are led to form as to what would be the composition of the molecule of the substance if it were obtained in the gaseous state. But it has yet to be proved that such "corrected normal" values, and those directly found for neutral compounds which can be gasified, uniformly represent the true molecular weights of the dissolved substances and not merely the weights of their fundamental molecules (cf. *these Proceedings*, 1889, 42).

Whereas in dilute solutions an excessive effect is often produced which would lead to the molecular weight being under-estimated if the result were at once accepted, in the case of concentrated solutions

a contrary result is frequently encountered, corresponding to more or less exaggerated estimates of the molecular weight: thus the effect produced by alcohol, for example, in a 32·5 per cent. solution is such as apparently to correspond to a molecular weight of 318 (Beckmann). It is not difficult to explain this result on the mechanical hypothesis of the nature of solutions; and still less difficult on the assumption that dissolution is in the main a chemical process: inasmuch as in concentrated solutions less opportunity is given for the molecules of the dissolved substance individually to exercise their specific effect; inasmuch as molecular aggregates are more likely to persist; and inasmuch as the solvent may consist no longer of the substance ostensibly employed as solvent, but in part, at least, of a compound of solvent and dissolved substance. The reduction of the specific effect and the consequent exaggeration of the molecular weight in the cases here contemplated may be said to be due to inter- if not to extra-molecular compensation.

But it is also conceivable that intramolecular compensation may take place, and that there may be compounds, the existence of which is not to be foreseen on the dissociation hypothesis, which exercise not an excessive but an inferior effect. The molecular weight of such compounds would necessarily be over-estimated by the application of the Raoult methods. Benzene and thiophen may be cited as mere illustrations of what is meant by internal compensation: benzene, it is well known, does not manifest the activity of a "triethylenic" compound, and evidently, in some manner not clearly understood, the six "surplus" affinities of the six carbon-atoms internally neutralise or compensate each other; in thiophen the sulphur appears to function only as a dyad, manifesting no tendency whatever to exhibit a higher valency in the manner so characteristic of sulphur in open-chain compounds: the inclusion of the sulphur in the chain in this case, therefore, involves a marked diminution in its activity.

It may be suggested that probably colloids generally are compounds of inferior activity, such as are contemplated on the view here put forward. It is well known that they diffuse with extreme slowness (cf. *Nature*, **35**, 598), and they are as a class very inert substances, the vapour-pressures of their aqueous solutions, for example, being almost if not the same as those of water alone at the same temperatures. The results recently brought forward by Brown and Morris for carbohydrates are of great interest, but it may be doubted whether they do more than confirm the views previously held with regard to the relative complexity of the several compounds. The same remark applies to the observations of Gladstone and Hibbert on caoutchouc. The fundamental molecule of a glucose must contain at least 6 carbon-atoms,

and that of a saccharon (any member of the cane-sugar group) 12; that of an amylin (or dextrin) therefore most probably contains at least 24 carbon-atoms. A variety of *amyloins* might well result from the conjunction of amylon (maltose) and amylin molecules in various proportions: maltodextrin, $C_{12}H_{22}O_{11}{\cdot}2C_{12}H_{20}O_{12} = C_{12}H_{22}O_{11}{\cdot}C_{24}H_{40}O_{20}$; inulin, $2C_{12}H_{22}O_{11}{\cdot}4C_{12}H_{20}O_{10} = 2C_{12}H_{22}O_{11}{\cdot}2C_{24}H_{40}O_{20}$; and amylodextrin, $C_{12}H_{12}O_{11}{\cdot}6C_{12}H_{20}O_{10} = C_{12}H_{22}O_{11}{\cdot}3C_{24}H_{40}O_{20}$, representing these by the formula assigned to them by Brown and Morris, are apparently such compounds. By duplication of the molecule and withdrawal of the elements of water from such amyloins, "higher dextrins" might be formed which would still be compounds of moderate molecular weight; and even simpler compounds would result if the amyloins were merely to lose the elements of water. Compounds thus formed would undoubtedly be less active than the parent carbohydrates, owing to the "cancelling" of the hydroxyl-groups; and it may well be that they would exercise an inferior effect in solution, and one such as is observed in the case of colloids.

It is undoubted that by the application of the Raoult methods a number of most interesting facts have been elucidated, which it is impossible and unnecessary to deny, but it is equally certain that we are only called on to make a rational use of them, and that slavish submission to the facts cannot be demanded. Those who directly accept the conclusions which are drawn, perhaps, have hardly realised what is involved, viz., adherence to the view that in a dilute aqueous solution of hydrogen chloride, for example, as much as 90 per cent. of the chloride is present, not as such but in the form of *free hydrogen and chlorine atoms:* such a conclusion may enable certain mathematical problems to be solved in an apparently satisfactory manner, but it is hardly one which a chemist's common sense would lead him to accept forthwith, in the absence of any explanation accounting for so extraordinary a difference between a dissolved substance at a low temperature and the same substance in the gaseous state at a high temperature. Attention may also be directed to the contradiction involved in the assumption that hydrogen chloride, although not appreciably dissociated when heated alone at 1500° in porcelain (Crafts and Meier), undergoes almost complete dissociation when dissolved in water, whereas nitrogen peroxide, according to Ramsay's experiments, exists in solution as N_2O_4, notwithstanding that it cannot be gasified unchanged, and is almost entirely resolved into NO_2 molecules at a temperature of about 200°.

Discussion.

Dr. Gladstone defended Raoult's freezing method, relying on the numerous coincidences between its indications and those afforded by

vapour-density determinations. In illustration he referred to the polymeric C_5H_8 hydrocarbons. Mr. Hibbert and he had found that each of these, when dissolved in benzene, gave a freezing point indicating an analogous molecular composition in the gaseous and dissolved condition. The conclusion from the small lowering produced by colloids that they have a very complex molecule is only in accordance with what has been long believed on chemical grounds. No doubt there are discrepancies and difficulties; but a careful consideration of these must serve to improve our knowledge of chemical and physical theory.

Mr. Hibbert said, that in applying Raoult's method, he had found it advantageous to surround the freezing vessel with an air chamber. The freezing point was then more definite.

The contention of Dr. Armstrong against the applicability of Raoult's method to colloid substances was based on objections to the dissociation theory of electrolysis. It might be true that the only argument in favour of that theory was the fact that the smallest electromotive force was able to produce decomposition in an electrolyte, but the argument was a very strong one, and commanded the assent of nearly every physicist in Europe. With reference to the effect of colloids on boiling point, &c., the question was whether they did or did not produce a real alteration. Recent researches seemed in favour of a positive result.

66. "The correspondence between the magnetic rotation and the refraction and dispersion of light by compounds containing nitrogen." By J. H. Gladstone, Ph.D., F.R.S., and W. H. Perkin, Ph.D., F.R.S.

The substances containing nitrogen, the magnetic rotation of which was described in Dr. Perkin's recent paper, have been examined by Dr. Gladstone with reference to their refraction and dispersion. The result is given in a table in which the molecular magnetic rotation, molecular refraction and molecular dispersion for 41 substances are placed in parallel columns with a view of drawing attention to the general correspondence that exists between these three different properties of the substances in question; a correspondence that points to some connection between the rotation of the polarised ray under magnetic influence and the retardation of the rays of light in passing through a material substance. Each property is governed by the following primary law. The molecular magnetic rotation, refraction or dispersion of a compound body, is the sum of the atomic magnetic rotation, refraction or dispersion of its constituents. The values which have been deduced under this primary law, are, however, subject to large modifications dependent upon differences in the structure of the compound.

The paper shows that when a change occurs in one property, it is noticeable also in the other two, and these changes are in the same direction, though not to the same extent; in fact, the variations in the magnetic rotation are usually greater than those in the dispersion, and these again are much more marked than in the refraction.

Eight sets of comparisons are given, each showing the correspondence in a different way :—

1. Compound ammonias. Ethylamines and propylamines, showing for each additional substitution a continuous augmentation of the value.

2. Hydrochlorides of the ethylamines, showing for each substitution a value smaller than the normal.

3. Methylanilines, showing a greatly increased value for CH_2.

4. Unsaturated compounds, allylamine, pyridine and aniline, showing a great increase upon the values for saturated compounds.

5. Propylamine compared with propionitril and trimethylene cyanide, showing two different values for nitrogen.

6. Nitric ethers, showing normal values for each CH_2, except the first.

7. Isobutyl nitrite and nitrate, showing the diminution of the nitrogen value with change of valency.

8. Acids and their ammonium salts, showing a superior value for acids in aqueous solution, and its continuance or partial disappearance on combination with nitrogen bases.

Apparent exceptions are mentioned, but the following is the general conclusion :—

It may be laid down as generally if not always true, that where there is a departure from the normal values in regard to one or other of these properties, it is to be found in the other two. The different properties are evidently similarly affected by change in chemical constitution. The general drift of the whole comparison appears to lead irresistibly to the conclusion that we have here another close relationship between electromagnetism and the velocity of light.

67. "Note on the oxidation of paradiamines." By R. Meldola, F.R.S., and R. E. Evans.

It is well known that quinones are formed by the oxidation of benzenoid paradiamines, and it is generally believed that the amido-groups are split off in the form of ammonia, but it does not appear that any quantitative determination of the amount of ammonia produced has been made. The authors have, therefore, made a series of experiments with paraphenylenediamine prepared by the reduction of paranitraniline, using the base in the form of the sulphate, this

salt being easily purified by crystallisation. After several preliminary trials, the most convenient mode of procedure was found to be as follows:—The calculated quantity of potassium dichromate was dissolved in water, and the solution of the diamine sulphate poured in; the mixture was allowed to stand for two days at the ordinary temperature, and then filtered to remove the quinone and its associated impurities. The filtrate was made distinctly acid with dilute sulphuric acid, and evaporated on a water-bath to a small bulk, then transferred to a flask, and made alkaline with caustic soda. The ammonia was driven off by a current of steam, and received in dilute chlorhydric acid. The distillate was evaporated to dryness in a weighed dish, and the dry residue weighed as ammonium chloride. 5 grams of paraphenylenediamine sulphate treated in this way gave 2·38 grams of ammonium chloride. The quantity required by theory is 2·6. The ammonium chloride was tested qualitatively, and found to be free from impurities.

68. "Monobenzyl-derivatives of the phenylenediamines." By R. Meldola, F.R.S., and J. H. Coste.

Monobenzylparaphenylenediamine was prepared by reducing monobenzylparanitraniline (Meldola and Salmon, Trans., 1888, 774) with tin and chlorhydric acid, and removing the tin as sulphide. The dihydrochloride, $C_6H_4{\cdot}NH_2{\cdot}NH{\cdot}C_7H_7{\cdot}2HCl$, forms lustrous, white scales readily soluble in water, less soluble in chlorhydric acid, and almost insoluble in alcohol. Ferric chloride gives a green coloration when added to the aqueous solution, this colour soon changing into red. The diacetyl-derivative, $C_6H_4{\cdot}NHAc{\cdot}NAc{\cdot}C_7H_7$, forms colourless, hexagonal prisms melting at 116·5—117°. The dibenzoyl-derivative forms white needles melting at 124°. One mol. prop. of the benzyldiamine oxidised in the presence of one of benzylaniline gives the dibenzylindamine, $C_7H_7{\cdot}HN{\cdot}C_6H_4{\cdot}N{:}C_6H_4{:}N{\cdot}C_7H_7$. This compound, which is of an intense greenish-blue colour with a coppery lustre, rapidly undergoes spontaneous decomposition, and becomes converted into what is apparently a mixture of benzylbenzylidene- and dibenzylidene-diamidodiphenylamine,

$$NH\begin{cases}C_6H_4{\cdot}N{:}CH{:}C_6H_5\\C_6H_4{\cdot}NH{\cdot}CH_2C_6H_5\end{cases} \text{ and } NH\begin{cases}C_6H_4{\cdot}N{:}CH{\cdot}C_6H_5\\C_6H_4{\cdot}N{:}CH{\cdot}C_6H_5\end{cases}.$$

One molecule of the benzyldiamine oxidised in the presence of two molecules of benzylaniline at the temperature of boiling water gives an azine or benzylated saffranine, which is of interest as being produced, in contradiction to the generally received view, from one molecule of a diamine and two molecules of a *secondary* monamine. The free amido-group of the benzyldiamine can be diazotised by the

action of nitrous acid, and the diazo-salts combine with phenols in the usual way to produce azo-compounds. Of the latter, the azo-derivatives of α- and β-naphthol have been prepared. The free base, benzylparaphenylenediamine, has been isolated, and forms reddish, moss-like, crystalline aggregations; the melting point is 30°; the base reddens by oxidation on exposure to the air. Monobenzylmeta-phenylenediamine was prepared in a similar manner to the above by reducing benzylmetanitraniline. The free base is oily at the ordinary temperature; the dihydrochloride forms dense laminated rhombohedra of an ochreous colour. The aqueous solution of the latter salt gives a red colour passing into orange-brown on the addition of ferric chloride. On heating the solution with ferric chloride, or other oxidising agent, a white, insoluble product of oxidation settles out. The diacetyl-derivative of the benzylmetadiamine forms an uncrystallisable resin; the dibenzoyl-derivative forms rhomboidal plates melting at 178°. By oxidising equi-molecular proportions of the benzylmeta- and benzylpara-diamines, a deep indigo-blue indamine is precipitated. This colouring matter is fairly stable in the cold, but passes into an azine on heating.

69. "Note on a yellow pigment in butterflies." By F. Gowland Hopkins.

For the most part the colour effects on the wings of lepidopterous insects are probably due to purely physical causes, and not to the presence of any definite pigment. But in some cases pigments are undoubtedly present. These are for the most part very difficult to isolate; but an exception to the rule occurs in the case of a certain yellow pigment which is found in its purest form in the common English brimstone butterfly. The pigment may also be detected in the wings of a very large number of day-flying lepidoptera. It may be obtained from the wings by simple treatment with hot water, in which it is freely soluble; and it may be identified by its yielding a marked murexide reaction when evaporated with nitric acid and afterwards treated with ammonia or potash.

The wings should be first treated with hot alcohol and ether, in which the pigment is insoluble, then boiled up with water, and the yellow aqueous solution filtered while hot. If the aqueous solution be now concentrated to a small bulk, and allowed to cool, the substance separates out as a yellow amorphous precipitate. It may be purified by dissolution in a fresh quantity of hot water, whence it again separates on cooling. Otherwise it may be removed from the wing by the action of dilute alkalis in the cold, and afterwards precipitated by the addition of acetic acid. The common brimstone butterfly yields

somewhat less than a milligram of pigment from each insect; larger foreign species, such as those belonging to the genus *Callidryas*, may yield as much as 4—5 milligrams.

The pigment is an amorphous powder, insoluble in alcohol, ether, chloroform, and all the more common organic solvents. It is very sparingly soluble in cold, but freely so in hot water.

Its aqueous solutions have a fine blue fluorescence and are strongly acid to litmus. The substance is freely soluble in alkalis, yielding with them solutions darker in colour than is its aqueous solutions; from these it is precipitated when neutralised with acetic acid.

It thus agrees closely in its physical properties with *mycomelic acid*, a yellow derivative of uric acid; though its yellow colour is more decided than is that of the latter substance. Mycomelic acid does not, however, yield a murexide reaction, while the pigment, as stated above, does so in a very marked manner. If it be boiled for some time with chlorhydric acid it is decomposed, and crystals of uric acid separate out, coloured much in the same manner as when obtained from acidified urine; on prolonged boiling with the dilute acid, urea is formed together with other crystalline substances not yet determined. There can be no doubt that the pigment is a derivative of uric acid, probably allied to mycomelic acid. It appears not improbable to the author that it may indeed be a condensation product of the two acids uric and mycomelic, and progress towards its synthesis has been made in this direction. If it be supposed that the two acids unite, with elimination of 2 mols. of water, to form a new dibasic acid, the acid would yield a silver compound containing 44·44 per cent. of silver. The pigment under discussion gives a perfectly definite silver compound, the amount of silver found in three analyses being 44·61, 44·66, and 44·42 per cent.

The author hopes shortly to obtain a sufficiency of the substance for accurate ultimate analysis.

70. "Zinc dextrosate." By A. C. Chapman.

This compound is prepared by dissolving zinc hydrate in the smallest possible quantity of ammonia solution and adding the liquid to a solution of dextrose in 90 per cent. alcohol; its composition is represented by the formula $C_6H_{12}O_6{\cdot}2ZnO{\cdot}3H_2O$.

71. "β-Bromonaphthalenesulphonic acid." By R. W. Sindall.

Whereas the two isomeric acids obtained on sulphonating β-chloronaphthalene by means of SO_3HCl—no heat being applied except in distilling off the carbon disulphide used as solvent of the chloronaphthalene—have been shown to correspond respectively to the so-called Badische and Brönner modifications of betanaphthylamine-

sulphonic acid, the 2 : 1′ being the chief, and the 2 : 3′ the subsidiary product; the experiments made by Mr. W. Houlding (*these Proceedings*, 1889, 74) have shown that in the case of β-iodonaphthalene the result is different, inasmuch as the β-iodo-acid prepared from the Brönner β-amido-acid is not identical with either of the two β-iodo-acids formed by direct sulphonation of β-iodonaphthalene. Mr. Houlding has shown that the bromo-acid prepared from the Brönner β-amido-acid is identical with the minor product of sulphonation of β-bromonaphthalene; to determine the nature of the major product of sulphonation, the author has prepared the isomeric acids from the three isomerides of Brönner's β-amido-acid.

2 : 1′ *Bromonaphthalene-α-sulphonic Acid.*—Although this acid has been prepared by Forsling (*Ber.*, 1889, 619), the account which he gives is insufficient for the purposes of comparison. The author finds, as was to be expected, that the bromo-acid prepared by the Griess-Sandmeyer process from the Badische β-amido-acid is identical with the major product of sulphonation of β-bromonaphthalene (cf. *these Proceedings*, 1887, 23). The sulphochloride melts at 147°; the sulphobromide, as stated by Forsling, at 151°; the sulphonamide melts at about 209°.

2 : 4′ *β-Bromonaphthalene-α-sulphonic Acid.*—This acid was prepared from the Dahl β-amido-acid. Its sulphochloride crystallises well from light petroleum in aggregates of small prisms melting at 77°; the sulphonamide melts at about 217°.

2 : 2′ *β-Bromonaphthalene-β-sulphonic Acid.*—Mr. Houlding had prepared this acid from the δ- (Bayer and Duisberg) amido-acid; the author has repeated the experiments. The sulphochloride crystallises from benzene in massive, oblique prisms melting at 100°; the sulphonamide melts at about 218°.

On distilling the sulphochlorides of the four β-bromo-acids with phosphorus pentachloride, the product obtained chiefly consists of the corresponding *dichloronaphthalene*, both the bromine atom and the SO_2Cl group becoming displaced by chlorine. In Mr. Houlding's paper (*loc. cit.*) the melting point 137° is wrongly assigned to 2 : 3′ chlorobromonaphthalene.

72. "Isomeric change in the naphthalene series. No. 5. β-Iodonaphthalenesulphonic acids." By Henry E. Armstrong and W. P. Wynne.

The authors describe the results obtained on carrying out the experiments referred to at the close of a recent communication by Mr. W. Houlding (*these Proceedings*, 1889, 74; cf. *supra*).

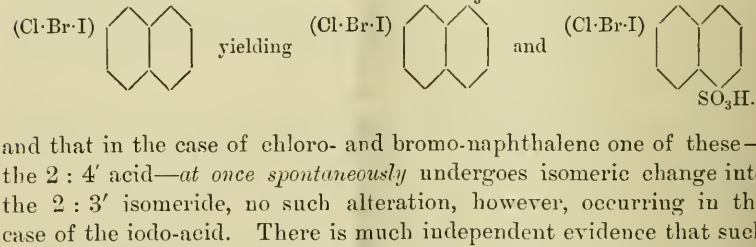
2 : 2′ *β-Iodonaphthalene-β-sulphonic Acid.*—This acid was prepared by Mr. Houlding from betanaphthylamine-δ-sulphonic acid. Its

sulphochloride crystallises from benzene in aggregates of small prisms melting at 100°; its sulphonamide melts at 210°. It is not identical with either of the acids produced on sulphonating β-iodonaphthalene.

2 : 1′ *β-Iodonaphthalene-α-sulphonic Acid.*—The authors have prepared this acid from the Badische modification of betanaphthylaminesulphonic acid, and find that, as was to be supposed, it is identical with the major product of sulphonation of β-iodonaphthalene by SO_3HCl. It is to be noted, however, that the sulphochloride melts at 164—165°, and not at 174° as by mistake has been previously stated (*B.A. Report*, 1887, 234). The sulphonamide melts at about 240°.

2 : 4′ *β-Iodonaphthalene-α-sulphonic Acid.*—On preparing this acid from the Dahl modification of betanaphthylaminesulphonic acid, it was found to be identical with the acid obtained as minor product on sulphonating β-iodonaphthalene by means of SO_3HCl. The sulphochloride melts at 92·5°; the sulphonamide at about 213°.

Although, therefore, the major product of sulphonation in the case of β-chloro-, bromo- and iodonaphthalene is the 2 : 1′ *alpha*-sulphonic acid, the minor product is different: β-iodonaphthalene yielding a second *alpha*-sulphonic acid, whereas β-chloro- and bromo-naphthalene each give the 2 : 3′ *beta*-sulphonic acid; and it should also be stated that a smaller proportion of the acid which is the subsidiary product is obtained both from chloro- and from bromo- than from iodonaphthalene. Two explanations of the dissimilarity are possible, viz.: either that there is an initial difference of behaviour; or that there is no initial difference, but that isomeric change takes place in the case of the chloro- and bromo-, and not in the case of the iodo-compound. The latter appears the more probable. It may be supposed that initially on sulphonation two isomeric acids are formed—



and that in the case of chloro- and bromo-naphthalene one of these—the 2 : 4′ acid—*at once spontaneously* undergoes isomeric change into the 2 : 3′ isomeride, no such alteration, however, occurring in the case of the iodo-acid. There is much independent evidence that such a change may well occur: thus on sulphonating 1 : 4 dichloronaphthalene a heteronucleal dichloro*beta*sulphonic acid is obtained as sole product; but there is every reason to believe that the actual product of sulphonation is an *alpha*-acid, and if this be the case isomeric

change must take place spontaneously, and with exceptional facility and completeness. 1 : 3 Dichloronaphthalene yields only an alpha-sulphonic acid. 1 : 2 Dichloronaphthalene, however, affords a mixture of about two-thirds 1 : 2 : 4′ *alpha*-sulphonic acid with one-third of the isomeric 1 : 2 : 3′ *beta*-sulphonic acid (cf. *these Proceedings*, 1889, 52); this latter the authors believe to be a product of spontaneous isomeric change occurring at the moment of sulphonation, and that this is the case is placed almost beyond question by the observation that if the mixed product of sulphonation be heated at 150—160° during 10 hours, the alpha-sulphonic acid almost entirely disappears, the beta-acid taking its place.

It has previously been shown that 2 : 1′ β-chloronaphthalene-α-sulphonic acid is converted into the 2 : 3′ acid by heating it at about 150° (cf. *these Proceedings*, 1887, 145). The 2 : 1′ iodo-acid should therefore be convertible into the 2 : 3′ isomeride, and this is found actually to be the case. The product obtained on sulphonating β-iodonaphthalene and then heating the resulting mixture of alpha-acids at 150° during about five hours, in fact, consists almost entirely of the 2 : 3′ iodo-acid identical with that prepared from the Brönner betanaphthylaminesulphonic acid, showing clearly that not only the 2 : 1′ but also the 2 : 4′ acid passes by isomeric change into the symmetric $\beta\beta$ 2 : 3′ acid.

73. "The formation of sulphones on sulphonating naphthalene-derivatives by means of chlorosulphonic acid." By W. M. Heller.

When naphthalene and its monohaloid derivatives are sulphonated by means of SO_3HCl, a varying but always small proportion of sulphochloride is usually obtained, but apparently this is a secondary product, and results from the action of the SO_3HCl on the sulphonic acid which is first formed.

On sulphonating 1 : 4 chlorobromonaphthalene, dissolved in carbon bisulphide, by SO_3HCl, using equimolecular proportions of the inter-agents, the author has found that the whole of the naphthalene compound is acted on, but that only a relatively small amount of sulphonic acid is obtained, the chief product being the sulphone, $(C_{10}H_5ClBr)_2SO_2$, no sulphochloride being formed. The corresponding β-dichloro- and dibromo-naphthalene behave similarly. The melting points of the sulphones thus obtained, and of the sulphochlorides prepared from the corresponding sulphonic acids, are as follows:—

$\beta Cl_2 \cdot SO_2Cl$	133°	Cl_2 sulphone about	216°
$\beta ClBr \cdot SO_2Cl$.	—	ClBr „	224
$\beta Br_2 \cdot SO_2Cl$	119°	Br_2 „	23

The sulphones are almost insoluble in benzene, but may be crystallised from xylene.

On sulphonating γ-dichloronaphthalene (m. p. 107°) by SO_3HCl, a small amount of a compound melting at 265° is obtained, which probably is also a sulphone. The corresponding chlorobromonaphthalene, however, appears to yield only sulpho-acid; the chloride of this acid melts at about 155°.

74. "Note on the hydration of cyanides." By Henry E. Armstrong.

Experiments made at the author's request by Mr. Houlding with the object of comparing the behaviour towards sulphonating agents of β-cyanonaphthalene with that of α-cyanonaphthalene have shown that, unlike the latter, the β-compound is not susceptible of sulphonation; if, however, it be dissolved in fuming sulphuric acid and the solution be cautiously poured into water, it is completely converted into β-naphthocamide, $C_{10}H_7{\cdot}CO{\cdot}NH_2$.

In like manner, Mr. Percival has found that on adding trichloracetonitril, $CCl_3{\cdot}CN$, to sulphuric anhydride, a liquid is obtained which gradually solidifies to a mass of crystals of a compound of the nitril with the anhydride; on adding this compound to water, it undergoes immediate and complete conversion into trichloracetamide.

These two cases appear to afford striking evidence in favour of the view that hydrating and hydrolytic agents act by forming compounds directly attackable by water; they serve, in fact, to support the integration rather than the dissociation hypothesis of chemical change. It is not improbable that the non-conversion of pentamethylbenzonitril into the corresponding acid to which Hofmann has called attention, and the recent similar observation made in Victor Meyer's laboratory (*Annalen*, **250**, 147) are to be explained as consequences of the incapability of the cyanides in question to form compounds with the hydrating agents used; and that perhaps sulphuric anhydride will be found available in these cases also.

75. "The existence of salicylic acid in certain genera of the *Liliaceæ*." By A. B. Griffiths.

The author states that he has isolated salicylic acid from the leaves, stems, &c., of *Tulipa*, *Yucca*, and *Hyacinthus* in the following manner:—

The leaves, stems, &c., cut up into small pieces, were digested with ether and the solution distilled. The residue was treated with distilled water and the solution filtered; the filtrate was then neutralised

with potassium carbonate, evaporated, and finally distilled with pure chlorhydric acid. The aqueous distillate yielded on evaporation colourless, prismatic crystals, which were found to be soluble in ether, alcohol, and boiling water, but sparingly soluble in cold water.

A solution of the crystals gave with ferric chloride a deep violet colour. A series of combustion analyses of these crystals were carefully performed, which he states gave the composition of salicylic acid. The crystals were found to melt at 131° C.; and on distilling them with lime, phenol and carbon dioxide were readily produced.

The author states that he has estimated the percentage of the acid in various parts of the plants with the following results :—

	Tulipa.	*Yucca.*	*Hyacinthus*
Leaves	0·0989	0·1410	0·1103
Peduncles	0·0812	—	0·0788
Stems	—	0·1065	—
Bulbs	0·0542	—	0·0483
Flowers	trace	—	trace

76. "On the oxidation products of acenaphthene." By T. Ewan, B.Sc., and J. B. Cohen, Ph.D., Owens College.

These experiments were undertaken with the view of preparing the products of the oxidation intermediate between acenaphthene and naphthalic acid.

By the action of lead oxide and water upon dibromacenaphthene bromide, a yellow crystalline compound melting at 126—129° was obtained, which has the formula $C_{12}H_4O_2Br_2$.

Acenaphthylene glycol monoacetate, $C_{10}H_6<\begin{matrix}CHOH\\ |\\ CH\cdot OC_2H_3O\end{matrix}$, is obtained by converting acenaphythlene dibromide into the acetate, and decomposing the product with potash; m. p. 122—122·5°.

Acenaphthylene glycol diacetate, $C_{10}H_6(CH\cdot OC_2H_3O)_2$, is obtained by boiling the monacetate with excess of acetic anhydride; m. p. 130°.

Acenaphthylene glycol is prepared by decomposing the monoacetate with boiling alcoholic potash. It crystallises in colourless needles, melting at 204—205°.

Acenaphthylene glycol monobenzoate is obtained by acting upon the dibromide with silver benzoate. It crystallises in plates melting at 189—190°.

Acenaphthene ketone, $C_{10}H_6<\begin{matrix}CH_2\\ |\\ CO\end{matrix}$, is prepared from the glycol by the action of sodium alcoholate. It crystallises in pale yellow needles melting at 119—119·5°.

The alkyl ethers of the glycol cannot be obtained by any of the usual reactions. If acenaphthylene bromide be acted on by sodium ethylate in alcoholic solution acenaphthene is formed, and if the bromide be treated with anhydrous sodium ethylate in benzene solution acenaphthylene is produced.

Tetrabromacenaphthene, $C_{12}H_6Br_4$, is formed by the action of bromine dissolved in carbon bisulphide upon acenaphthylene bromide; m. p. 161—162°.

Tribromacenaphthene, $C_{12}H_7Br_3$, is prepared in a similar manner; m. p. 88—90°.

Chromium oxychloride interacts with acenaphthene in solution in CS_2, and forms a well-defined addition compound, but the diketone could not be obtained. The authors have prepared crystalline compounds by distilling the barium salt of naphthalic acid with the lime salt of the fatty acids, which are probably the aldehyde and ketone-derivatives of naphthalic acid. Acenaphthene interacts with the acid chlorides in presence of aluminium chloride, forming ketones.

A crystalline compound has also been obtained by the action of PCl_5 upon naphthalimide. The investigation of these compounds will form the subject of a subsequent communication.

77. "Schützenberger's process for the estimation of the oxygen dissolved in water." By Sir Henry E. Roscoe, F.R.S., D.C.L., LL.D., and Joseph Lunt, B.Sc., Associate of the Owens College.

The authors find that a series of estimations made on the same sample of London tap water give results which differ 35 per cent. from the mean value, and that the time taken in titrating has a great influence, much higher results being obtained if titration be quickly than if it be slowly performed. The disturbing influence has been traced to the fact that when aerated water is introduced into an atmosphere of hydrogen as in the usual process, it immediately begins to lose oxygen by diffusion, a fact hitherto overlooked. The result of an oxygen estimation thus depends on the degree of exposure to hydrogen during titration, and results between 0·53 and 7·56 were obtained with the same water by varying the exposure.

Under favourable circumstances 20 per cent. of the dissolved oxygen diffuses, whilst in the usual form of the apparatus 50 per cent. of the oxygen diffuses during the estimation. An exposure of three minutes is sufficient to permit all the dissolved oxygen to escape. This explains the return of the blue colour during an estimation carried out in the usual manner, the *diffused* oxygen becoming reabsorbed by the reduced indigocarmine. No return of the blue colour takes place on reducing indigocarmine when free oxygen is absent, and the action has been

proved to be due to the supernatant gas, and not to any action occurring within the liquid as Schützenberger supposed.

Diffusion also explains the observation made by Schützenberger that twice the amount of oxygen is found when a large amount of reduced indigocarmine is present; in that case the dissolved oxygen is at once acted on and so cannot diffuse.

Ramsay and Williams, who have investigated the process, do not obtain twice the amount, but only an increase in the ratio 3 : 5. Diffusion also explains this observation, a smaller vessel having been used in their experiments a larger proportion of the oxygen was found in the usual process, in other words, three-fifths of the whole.

The method adopted to eliminate this error, due to diffusion, is to run the aerated water beneath the surface of a liquid containing a measured excess of hyposulphite, and a little reduced indigocarmine as an indicator. In this way the dissolved oxygen is immediately acted on by the hyposulphite and its diffusion prevented. For the standardisation of the hyposulphite, the two methods hitherto used were found inaccurate. The copper method being fundamentally wrong owing to a secondary action which occurs between sulphite and dissolved oxygen. The aerated distilled water method, hitherto used with Bunsen's absorption coefficients, the authors show to be inaccurate, giving the values obtained by them, which agree closely with observations made by Dittmar.

The new method of carrying out the process and the corrected values for the oxygen dissolved by distilled water give results for which perfect accuracy cannot be guaranteed, but which are not far removed from the truth, and certainly valuable. The reaction is much disturbed by the presence of free acid or alkali.

78. "Isomeric change in the phenol series" (third notice). By Arthur R. Ling.

The author finds that chlorine under a variety of conditions does not affect the conversion of ortho- into para-nitrophenol-derivatives; bromine alone appears to have this property.

He corrects a previous statement that orthochloroparabromorthophenol is converted by the action of bromine into parachlororthobromorthonitrophenol.

On treatment with nitric acid parachlororthobromorthonitrophenol yields parachlorodiorthonitrophenol, whereas parabromorthochlororthonitrophenol is converted into orthochloroparadinitrophenol—the bromine and not the chlorine atom being always displaced.

Orthochloroparabrom*orthonitro*phenol appears to undergo isomeric change when treated with bromine, yielding the isomeric ortho-

chlororthobrom*paranitro*phenol together with orthochlordinitrophenol and chlorotribromoquinone.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

A System of Chemistry, by J. Murray. Four vols. Edinburgh 1806–7. From G. W. Arnott, Esq.

Seventh Annual Report of the Board of Control of the New York Agricultural Experiment Station for the year 1888. Albany 1889. From E. F. Ladd, Esq., Chemist to the Station.

An Elementary Treatise on Heat, by H. G. Madan. London 1889. From the Author.

Commercial Chemical Analysis, by A. H. Allen. Second Edition. Vol. III. Part 1. London, 1889. From the Author.

La chimie à la ferme, par R. Warington. Traduit de l'Anglais par P. De Vuyst et P. Wanters. Bruxelles et Paris 1889. From the Author.

Der Ursprung und die Entwickelung der organischen Chemie, von C. Schorlemmer. Braunschweig 1889. From the Author.

Le fer dans la végétation, par P. Marguerite-Delacharlonny. Paris 1888. From Dr. A. B. Griffiths.

Report to the Science and Art Department on the Action of Light on Water Colours, by W. J. Russell and W. de W. Abney. London 1888. From Capt. W. de W. Abney.

U.S. Department of Agriculture: Division of Chemistry. Bulletin No. 13. Foods and Food Adulterants: Part 4. Lard and Lard Adulterations, by H. Wiley. Washington 1888. From J. M. Rusk, Esq., Secretary of Agriculture.

II. *By Purchase.*

Manuel pratique de Cristallographie, par G. Wyrouboff. Paris 1889.

Die Untersuchungen der Fette, Oele, Wachsarten und der technischen Fettproducte, von C. Schaedler. Erste Lieferung. Leipzig 1882.

Die Farbstoffe des Chlorophylls, von A. Hansen. Darmstadt 1889.

Zur Erinnerung an vorangegangene Freunde. Gesammelte Gedächtnissreden, von A. W. von Hofmann. Drei Bände. Braunschweig 1889.

HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY, ST. MARTIN'S LANE.

Issued 16/11/1889.

ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 72. Session 1889–90.

Titles of Papers received and printed in the Transactions during the recess.

79. "Contributions to the chemistry of the Azonaphthols." By Raphael Meldola, F.R.S., and Gilbert T. Morgan.

80. "The synthesis of heterogeneous mixed Alkyldiazoamido-compounds." (Preliminary Notice.) By Raphael Meldola, F.R.S.

81. "Benzophenylhydrazine." By S. Ruhemann, Ph.D., M.A., and F. F. Blackmann, B.Sc.

82. "Further study of the Thiocarbimides." By Augustus E. Dixon, M.D., Assistant Lecturer in Chemistry, Trinity College, University of Dublin.

83. "Benzylammonium Succinates and their derivatives." By A. Emil Werner, F.I.C., Assistant in the Chemical Laboratory of the University of Dublin.

84. "The dissociation of Amine vapours." By G. J. Burch, B.A., and J. E. Marsh, B.A., University Laboratory, Oxford.

85. "The Resin of *Myoporum Platycarpum*." By J. H. Maiden, F.L.S., Curator of the Technological Museum, Sydney.

86. "The lowering of the freezing point of Sodium by the addition of other Metals." By C. T. Heycock, M.A., and P. H. Neville, M.A.

November 7th, 1889. Dr. W. J. Russell, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. John Burgess, 7, Wellington Road, Peckham; William Frederick Britcher, 33, Tranquil Vale, Blackheath; Frank Hill Perry Coste, Ravenshoe, Burnt Ash Hill, S.E.; David Brown Dott, 104, South Canongate, Edinburgh; Robert Stephen Edwards, B.A., Gwern-y-Gaseg, Minera, Wrexham; James Kerr Erskine, 6, Lascotts Road, Wood Green, N.; John Foggie, Newport, Fifeshire, N.B.; Harold Gripper, 77, Cecil Street, Greenhays, Manchester; H. B. Helbing, German Hospital, Dalston; Robert Edward Hughes, 15, Clare Street, Canton, Cardiff; James Robert Kaye, 33, Great Charles Street, Birmingham; Henry Richard Kerwood, M.B., Frogmore Broadelyst, Devonshire; Frederick Thomas Knott, The Laurels, Eltham Road, Lee, Kent; L. Napier Levingham, Brightside Steel Works, Sheffield; G. B. Mason, Barbados, West Indies; James Braik Mason, 3, Park Terrace, Dundee; Thomas Mercer, Great Hey, Edersfield, near Bury, Lancashire; Joseph Alfred Nettleton, East Grinstead, Sussex; Wallace Christopher Nickels, 14, Yew Grove, Cricklewood, N.W.; James Gordon Parker, Penketh, near Warrington; Alfred Edridge Pike, Westminster Medical School, S.W.; William Ping, 2, Sandbourne Road, Brockley, S.E.; Frederick Quincke, Ph.D., 13, Portland Terrace, Regent's Park, N.W.; Sidney Augustus Sworn, 3, Peel Street, Bedford; Willis G. Tucker, M.D., Albany, N.J., U.S.A.; Daniel Walker, School of Mines, Ballarat, Victoria; Matthew Whittam, St. Peter's School, York; Basil P. Wigan, Macclesfield; John Wilkie, 20, Buckingham Street, Charing Cross; John Wiltshire, Knowsley Cottage, Torre Park, Torquay.

The following papers were read:—

87. "Isolation of a tetrahydrate of sulphuric acid existing in solution." By S. U. Pickering.

The freezing points of mixtures of sulphuric acid and water form three distinct curves, representing the crystallisation of water, of $H_2SO_4{\cdot}H_2O$ and of sulphuric acid respectively: in each of them the highest point is in exact correspondence with the composition of the substance which crystallises out. No solutions containing between between 75 and 40 per cent. of acid had yet been frozen, but it appeared to the author that if his former deductions from the irregularities in the curves representing the densities and other properties of solutions of the acid were correct, an independent curve represent-

ing the crystallisation of a new hydrate should occupy this interval, and that this new hydrate could only be either $H_2SO_4 5{\cdot}5H_2O$ or $H_2SO_4 4H_2O$. Experiment has proved that it is the latter. The two branches of the new curve obtained rise from about $-80°$, and meet in a sharply marked angle at a point exactly corresponding to the composition of the tetrahydrate, the temperature at which this point is reached being $-25°$. The tetrahydrate forms large, well defined, hard crystals.

Apart from the consideration that the isolation of this hydrate was the direct outcome of his having previously recognised its existence in the dissolved state, the author maintains that the crystallisation of a substance from a liquid necessitates the recognition of its existence in that liquid. The various possibilities are (1) that the solid constituents solidify separately in the proper proportions, and subsequently combine: this view is obviously untenable; (2) that the molecular aggregates constituting the solid are formed directly from the acid and water: this means that a hydrate has no fundamental molecule, and besides leaves the impossibility of explaining how these solid aggregates can hunt each other out, and congregate to form large crystals; (3) that fundamental molecules of the hydrate are formed in solution, but cannot remain there, and, consequently, separate out almost immediately: this is tantamount to saying that the hydrate is an insoluble substance, a proposition which could scarcely be maintained even if the substance were not crystalline; (4) that the molecules of the hydrate are formed in the liquid, and exist there till the temperature is lowered below its freezing point. This, in the author's opinion, is the only tenable hypothesis.

When a liquid freezes and melts at a definite temperature; when the temperature remains constant till the whole of the liquid is frozen; when any alteration in its composition lowers its freezing point: we have the most certain evidence yet adduced for regarding that liquid to be a definite, though, possibly, somewhat dissociated, compound. If we deny this argument as applied to the hydrate in question, we must deny it in all cases, and conclude that no liquid is a definite substance.

The author does not argue that the mere fact of the existence of the liquid hydrate at $-25°$ implies its existence at the higher temperatures (8—38°) at which his density and other determinations were made; on the contrary, he argued that because it existed at the higher temperatures it must exist at the lower ones, and, having proved this to be a fact, he holds that the premisses from which his conclusions were drawn must be correct.

The author believes that the dihydrate may yet be obtained as a

solid, since there is a reach of 7 per cent. in its vicinity where freezing points have not yet been attained. He has also isolated another hydrate which crystallises in small quantities with the monohydrate, but has not succeeded in determining its composition.

88. "Additional observations on the magnetic rotation of nitric acid and of hydrogen and ammonium chlorides, bromides and iodides in solution." By W. H. Perkin, Ph.D., F.R.S.

In his previous experiments (*cf.* these Proceedings, 1889, p. 83) the author had limited his observations on nitric acid to the pure acid, HNO_3; he has now examined a somewhat diluted acid, and the results obtained indicate that HNO_3 unites with water, forming an acid analogous to orthophosphoric acid, viz., $(HO)_3NO$.

The experiments on hydrogen chloride, bromide and iodide were originally made on single samples in a very concentrated solution of each. These gave abnormally high results—rather more than twice the values calculated for the pure compounds—but on examining solutions of different strength it was found that the rotation *increases* up to a dilution equivalent to about 6 or 7 mols. of water to 1 mol. of hydride, the value then remaining practically stationary. To see whether the solvent had any influence, a solution of hydrogen chloride in isoamyl oxide was examined, and was found to give values nearly identical with those calculated from the chlorine derivatives of the paraffins; and there can be little doubt that if the other hydrides could be examined in a similar way analogous results would be obtained. As union with water should reduce the rotations, the results at present are quite inexplicable.

The compounds with ammonia and the compound ammonias have been also further examined; the results are remarkable when considered in relation to those afforded by the hydrides, as the rotations found, instead of being those calculated from the results obtained in the case of paraffin-derivatives, or those *found* in the case of hydrogen chloride dissolved in isoamyl oxide, nearly correspond to those required on the asssumption that the hydrides are present in aqueous solution together with ammonia. The rotations, however, do not vary with the strength of the saline solutions. The author's explanation of this is that when the salts are dissolved in water they dissociate almost entirely into the hydride and the amine, the hydride undergoing an increased rotation on account of its being in aqueous solution. In the case of triethylamine chlorhydride the numbers are lower, and there is evidently less dissociation; and in the case of tetrethylammonium chloride little or no dissociation appears to take place. Solutions of ammonium iodide and diethylamine chlorhydride

in absolute alcohol gave somewhat lower numbers than aqueous solutions, indicating a somewhat smaller although large amount of dissociation.

As already noticed, ammonium nitrate gives numbers very close to the calculated; apparently it does not dissociate to any appreciable extent. As the author was not satisfied with the numbers obtained for neutral ammonium sulphate, the acid sulphate was examined, and this gave the calculated numbers; these, when compared with those for the neutral salt, show that the latter undergoes dissociation to a small extent when in solution, which is in agreement with the well-known fact that its solution in water gives off ammonia when heated. The examination of these oxy-salts shows clearly that the salts containing hydrogen chloride, bromide and iodide, when in aqueous solution, are in a very abnormal condition, but a condition which is easily explained if they are in a state of dissociation.

Discussion.

Dr. Gladstone said that when the refraction equivalents of the hydrides of the halogen elements and of nitric and sulphuric acids in solution were first determined, it was observed that the values were far higher than those calculated; but on re-examining hydrogen chloride solutions he had recently found that as the amount of water was increased a slight increase in the specific refraction also set in quite analagous to that described by Dr. Perkin. The whole subject of the behaviour of such substances in solution deserved a full and deliberate investigation with reference especially to the possible occurrence of dissociation. He had little doubt that some dissociation did occur in the case of the ammonium salts. As it is well known that increase of temperature greatly promotes dissociation, it would be well to repeat the observations at various temperatures in order to learn whether a change takes place in the refraction and magnetic rotation. On examining Dr. Perkin's solution of hydrogen chloride in amyl oxide, he found that the refraction and dispersion values deduced for the chloride are very much smaller than those afforded by aqueous solutions: thus another case of correspondence between the three properties of magnetic rotation, refraction and dispersion of light was made evident.

Professor Ramsay, referring to the high values observed by Dr. Perkin in the case of dilute solutions, drew attention to recent speculations concerning the occurrence of atomic dissociation in solutions, and asked, might not the high values be explained by assuming that hydrogen chloride underwent dissociation into hydrogen and chlorine atoms?

Dr. Armstrong said that although it might be argued from the results obtained with aqueous solutions that atomic dissociation attended dilution, the fact that normal values were obtained when amyl oxide was used as solvent was evidence of the insufficiency of such an explanation, and clearly indicated that the water played an active part; according to the now fashionable dissociation hypothesis, the solvent acted merely as a diluent, as one gas does to another, dilution corresponding to reduction of pressure; on this hypothesis, therefore, the values obtained should be the same for solutions of equivalent strength in either solvent. Dr. Perkin's results appeared to indicate that a certain proportion of the water molecules—those which were carried round, as it were, by the hydrogen chloride molecules—underwent what might be termed *extra* rotation. Dr. Perkin based his conclusion that hydrates would afford lower and not higher values on the results which he had obtained in the case of compounds such as the hydrates of nitric and sulphuric acids, and of aldehyde and of chloral; but these were all hydrates of compounds containing polyad elements: the behaviour of mixed elements might well be peculiar. In fact, in discussing these questions valency must be taken carefully into consideration. Dr. Gladstone had suggested that observations should be made at various temperatures; such observations would undoubtedly be of importance, and might even be expected to afford a final settlement in favour of one or the other hypothesis. If the increased rotation be conditioned by hydrates, as such hydrates would undergo dissociation on heating, the values would diminish as temperature rose; but if atomic dissociation took place, the change would be in the contrary direction, although, as the effect of temperature in promoting atomic dissociation is often not very marked until a somewhat high temperature is attained, the effect of moderate heating would not necessarily be exhibited by an increase of the rotation.

89. "Phosphoryl Trifluoride." By T. E. Thorpe, F.R.S., and F. J. Hambly.

The authors find that phosphorus oxyfluoride, POF_3, may be easily and conveniently made by heating a mixture of cryolite and phosphoric oxide, and collecting the products at the mercurial trough. The interaction appears to be strictly analogous to that by which Kolbe and Lautemann obtained phosphorus oxychloride by heating phosphoric anhydride with common salt; $2P_2O_5 + 3NaCl = POCl_3 + 3NaPO_3$ (*Ann. Chem. Pharm.*, **113**, 240).

90. "Acetylation of Cellulose." By C. F. Cross and G. T. Bevan.

By heating cotton cellulose with acetic anhydride and zinc chloride (Franchimont, *Ber.*, **12**, 2059), the authors have obtained a product which, judging from the results of analysis and the proportion of acetic acid which it yields when submitted to alkaline hydrolysis, appears to be a *pentacetyl* derivative of cellulose; the yield was found to be 83 per cent. of that calculated for a pentacetate, and the insoluble product of hydrolysis exhibited the behaviour of a normal cellulose. The compound is very stable, being reprecipitated unchanged from its solution in a mixture of nitric and sulphuric acids. It would appear therefore that all the oxygen of the cellulose molecule acts as hydroxylic oxygen. In discussing the bearing of these results, it is pointed out that the evidence upon which substitution of OH in the cellulose molecule has been assumed to be at a maximum with the triacetate (Schutzenberger) and trinitrate, is insufficient. Franchimont's representation of the molecule of cellulose as an aggregate of "glucose" groups, condensed according to the equation $n(C_6H_{12}O_6)-(n-1)H_2O$ (R.T.C. **2**, 241), is based upon strong evidence, but affords no suggestion of the mode in which the condensation takes place. The extreme inertness of cellulose, as evidenced by the fact that it does not interact with acetic anhydride at its boiling point, but only at a temperature of 180°; its resistance to the powerfully hydrolytic action of acid sulphites at high temperatures; together with the results detailed in this communication, go to show that it is probable that cellulose represents a type of carbon compound *sui generis*.

Discussion.

Dr. Armstrong remarked that present ideas as to the constitution of cellulose are mainly an extension of our views concerning carbohydrates of the cane-sugar and dextrin-groups: we are accustomed to regard these latter as etheric-derivatives of the glucoses, and to look on cellulose as a compound of a somewhat similar type; but its physical properties, its behaviour on acetylation, and the peculiar condition under which alone it undergoes hydrolysis serve to indicate that perhaps it is a compound of a different and special type, as the authors of the paper suggest may be the case. In seeking to formulate the constitution of cellulose, the possibility that it may even be a closed chain compound should not be entirely overlooked, the occurrence of compounds such as inosite and quinic acid—both derivatives of hexhydrobenzene—in plants being not without significance from this point of view.

91. "Action of light on moist oxygen." By Arthur Richardson.

The author finds that the presence of liquid water very much facilitates the oxidation of many substances under the combined influence of sunlight and oxygen. If, however, the water is present as aqueous vapour, the decomposition is exceedingly slow, and in some cases is entirely arrested.

He finds that peroxide of hydrogen is formed when water containing pure ether is exposed to light in an atmosphere of oxygen; on shaking some of the ether with a solution of potassium bichromate, the ether at once assumed a decided blue colour.

From an extended series of experiments the following facts have been observed:—(1.) The amount of hydrogen dioxide formed depends on the proportion of ether to water present. (2.) No dioxide is formed when a mixture of water vapour, ether vapour and oxygen is exposed to sunlight. (3.) No dioxide is formed when water and ether are exposed in an atmosphere of carbon dioxide. (4.) No iodine is liberated from potassium iodide by a mixture of water, ether and oxygen from which light has been excluded.

On exposing pure water, acidified with pure sulphuric acid, to light, hydrogen dioxide was found in the solution; this was estimated by permanganate of potassium. Water exposed to rays of low refrangibility gave no hydrogen dioxide.

On placing water which contained the dioxide, immediately after exposure to light, in the dark, it was found, after some time, to be free from dioxide; but hydrogen dioxide was formed on again exposing the solution to light; this process could be repeated indefinitely.

From these and other experiments the author is led to believe that the oxidation of substances under the influence of light involves in many cases initially an oxidation of water to hydrogen dioxide, and that the oxidation of the compound is the result of a secondary interaction between it and the hydrogen dioxide.

Discussion.

Dr. Armstrong said that it had long since been stated that peroxide of hydrogen was formed when ether and water was exposed to atmospheric oxidation; Mr. Kingzett had brought the subject under the notice of the Society several years ago (cf. *Chem. Soc. Journ.*, Abstr., 1877, p. 183). Dr. Richardson assumed that the water was directly oxidised; Mr. Kingzett had argued—and in the case of turpentine had adduced weighty experimental evidence—that the hydrogen peroxide was a secondary product, formed by the action of water on an organic peroxide. It was impossible to say from Dr.

Richardson's results which explanation was the correct one; perhaps neither was wholly correct, as it was not impossible that the conjoint influence of the water and ether was an essential feature of the interchange with oxygen. Dr. Richardson had added ether or sulphuric acid with the object of protecting the peroxide from decomposition; surely weak solutions of hydrogen peroxide were not so unstable that proof could not be obtained of its formation if it really were produced on exposing water and oxygen to light. There was no satisfactory evidence that it was formed in the absence of a third substance. In the case of the experiments made without ether, it was just possible that the minute amount of organic matter present in the water—perhaps that derived from stoppers—had been effective in promoting peroxidation; the disappearance of the peroxide in the dark tended to favour this view.

Professor Thorpe said that he had recently had occasion to satisfy himself that water played an important part in promoting peroxidation. It had long been known that the atmospheric so-called ozone reactions were at least principally due to hydrogen peroxide; finding in the Admiralty instructions the statement that the air of the Hebrides was said to contain more ozone than any air in the world, he had during a recent yachting tour there exposed Schönbein paper at various distances above sea level; he had always found that after six hours' exposure the "ozone" manifestations were very much stronger 5 or 6 feet above the sea than some distance above the sea, at the mast-head of the yacht.

Professor Ramsay drew attention to the fact that when a substance capable of destroying hydrogen dioxide was present, the peroxide might be formed and immediately thereafter destroyed. Such was probably the case in polluted rivers; and it might well be that the continual formation and decomposition of hydrogen peroxide was the effective cause of the oxidation of organic matters in waters. Its formation apparently tended towards a maximum, which in presence of matter capable of decomposing it would never be reached (cf. these Proceedings, 1886, p. 225).

Mr. Groves remarked that weak solutions of hydrogen peroxide were by no means unstable, but would keep for months.

Professor Dunstan asked whether Dr. Richardson had proved that the oxidising substance was hydrogen peroxide. He had made a series of experiments which showed that it was not formed when *pure* ether was used, although a substance was produced which was capable of liberating iodine.

Dr. Thorne, referring to the possible effect of a third substance in influencing oxidation, said that he had had occasion to observe that in bleaching coloured fibres a solution of 75 per cent. strength of hypo-

chlorite in presence of oxygen gave the same results as one of 100 per cent. strength used alone.

The question was asked whether the precaution had been taken in the experiments with potassium iodide to exclude carbon dioxide from the air.

The President said that in experiments which he and Captain Abney had made together on the fading of water colours, the action of aqueous vapour had been most strikingly apparent; colours were found to be stable on exposure to light in dry air which were considerably affected when aqueous vapour was present.

Dr. Richardson, replying, said that the bichromate test indicated that the substance formed in presence of ether was hydrogen peroxide. Using pure water, he had obtained traces of peroxide, which, however, could not be estimated. In some cases the bottles in which the exposure to light was effected were provided with glass stoppers. He thought that very little was known as to what happens when iodine separates from potassium iodide: the solution does not exhibit an alkaline reaction.

92. "$\alpha\beta$-Dibenzoylstyrolene and the constitution of Zinin's lepiden derivatives." By Francis R. Japp, F.R.S., and Felix Klingemann, Ph.D.

In a preliminary note (*Ber.*, **21**, 2933) the authors showed that by the action of iodhydric acid on $\alpha\beta$-dibenzoylstyrolene (anhydracetophenonebenzil) triphenylfurfuran was formed:—

$$\begin{array}{l} C_6H_5\cdot C{=}CH \\ C_6H_5\cdot CO\ CO\cdot C_6H_5 \end{array} + 2H = \begin{array}{l} C_6H_5\cdot C{-}CH \\ C_6H_5\cdot C\quad C\cdot C_6H_5 \\ \qquad\quad \backslash O / \end{array} + H_2O.$$

An attempt to prepare the corresponding dibenzoylstilbene,

$$\begin{array}{l} C_6H_5\cdot C{=}C\cdot C_6H_5 \\ C_6H_5\cdot CO\ CO\cdot C_6H_5 \end{array},$$

in order to convert it by the action of iodhydric acid into tetraphenylfurfuran, failed; but the authors pointed out (*ibid.*, p. 2934, footnote) that possibly Zinin's lepiden, $C_{28}H_{20}O$ (m. p. 175°) was the desired tetraphenylfurfuran. In making this suggestion, it had escaped their notice that a similar idea had been put forward by Dorn as early as 1870 (*Annalen*, **153**, 358), Dorn calling lepiden "oxyphenyltetrol," and ascribing to it the formula

$$\begin{array}{l} C_6H_5\cdot C{=}C\cdot C_6H_5 \\ C_6H_5\cdot C{-}C\cdot C_6H_5 \\ \qquad\quad \backslash O / \end{array}.$$

Magnanini and Angeli (*Ber.*, 22, 853) have since found that Zinin's hydro-oxylepiden is identical with Knoevenagel's bidesyl,

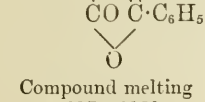
$$\begin{array}{l} C_6H_5\cdot CH-CH\cdot C_6H_5 \\ C_6H_5\cdot CO \quad\ CO\cdot C_6H_5 \end{array};$$

and by the dehydrating action of chlorhydric acid they have converted bidesyl into tetraphenylfurfuran identical with lepiden. They regard Zinin's oxylepiden, $C_{28}H_{20}O_2$, as having the formula of the before-mentioned dibenzoylstilbene. This view would make oxylepiden a strict analogue of dibenzoylstyrolene: as dibenzoylstilbene it is phenyldibenzoylstyrolene.

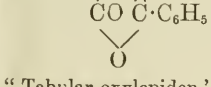
The authors have been engaged for some time in studying the interactions of dibenzoylstyrolene, and find, in support of the foregoing view, that there is an almost perfect parallelism in behaviour between it and oxylepiden. The various compounds obtained by them stand to the corresponding compounds of the lepiden series in the relation of triphenyl-derivatives to tetraphenyl-derivatives, a relation which is exhibited, in the first place, in the case of dibenzoylstyrolene and oxylepiden themselves. It is necessary to point out, however, that, of the three "oxylepidens" prepared by Zinin, the analogue of dibenzoylstyrolene is "acicular oxylepiden" (m. p. 220°).

By heating "acicular oxylepiden" with iodhydric acid, Berlin (*Annalen*, 153, 131) converted it into lepiden (tetraphenylfurfuran). As already mentioned, the authors have shown that when subjected to the same treatment dibenzoylstyrolene yields triphenylfurfuran.

By heating "acicular oxylepiden" Zinin obtained two isomeric "oxylepidens:" as chief product "tabular oxylepiden" (m. p. 130°), and in small quantity "octahedral oxylepiden" (m. p. 232°). In like manner, by heating dibenzoylstyrolene the authors have converted it into two isomerides: a compound formed in large quantity, crystallising from alcohol in long, lustrous needles, melting at 117—118°, corresponding with "tabular oxylepiden;" and a compound formed only in small quantity, crystallising from alcohol, in which it is very sparingly soluble, in slender, white needles, melting at 197—198°, corresponding with "octahedral oxylepiden." They regard the compound melting at 117—118° as *triphenylcrotolactone*, and "tabular oxylepiden" as *tetraphenylcrotolactone*:—



Compound melting at 117—118°.

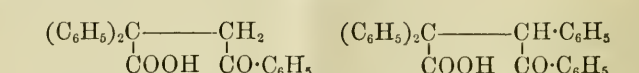


"Tabular oxylepiden."

On oxidation with excess of chromic anhydride, triphenylcroto-

lactone yields benzophenone and benzoic acid. Zinin does not appear to have oxidised "tabular oxylepiden," but he obtained benzophenone from isolepiden, which is formed from "tabular oxylepiden" by distillation.

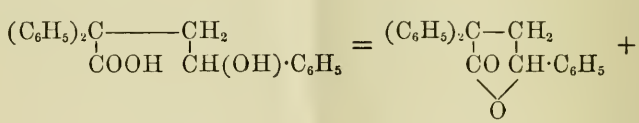
Caustic potash in alcoholic solution converts triphenylcrotolactone into a salt of *α-diphenyl-β-benzoylpropionic acid.* Zinin has shown that "tabular oxylepiden" yields oxylepidenic acid, $C_{28}H_{22}O_3$, when similarly treated. The following formulæ express the authors' views as to the constitution of these two acids :—



α-Diphenyl-β-benzoylpropionic acid (m. p. 182—183°).

Oxylepidenic acid.

Diphenylbenzoylpropionic acid displays the behaviour of lævulic acid and other γ-ketonic acids. Thus it interacts with phenylhydrazine with elimination of *two* mols. of water, yielding the compound $C_{28}H_{22}N_2O$ (m. p. 185°). In a similar manner, hydroxylamine converts it into the compound $C_{22}H_{17}NO_2$, melting at 150—152°. Nascent hydrogen reduces it to a γ-hydroxy-acid, which is very unstable, and when liberated from its salts, speedily parts with water, yielding a lactone :—



Triphenyl-γ-hydroxybutyric acid.

Triphenylbutyrolactone (m. p. 153°).

This lactone may also be obtained directly from triphenylcrotolactone by boiling it with iodhydric acid.

When heated above its melting point, diphenylbenzoylpropionic acid is reconverted with loss of water into triphenylcrotolactone, a process which corresponds with the formation of the anhydrides of lævulic acid, observed by Wolff (*Annalen*, **229**, 249). Zinin has shown that oxylepidenic acid can be reconverted by the dehydrating action of heat into "tabular oxylepiden."

Zinin's "octahedral oxylepiden" and the corresponding compound melting at 197—198°, obtained from dibenzoylstyrolene, are difficult to prepare in quantity, and have not yet been fully examined; but the authors incline to the view that these compounds are stereometric isomerides of "acicular oxylepiden;" and αβ-dibenzoylstyrolene respectively, and would classify them as follows :—

Maleoid form.	*Fumaroid form.*
" Acicular oxylepiden."	" Octahedral oxylepiden."
$\alpha\beta$-Dibenzoylstyrolene	Iso-$\alpha\beta$-dibenzoylstyrolene
(m. p. 129°).	(m. p. 197—198°).

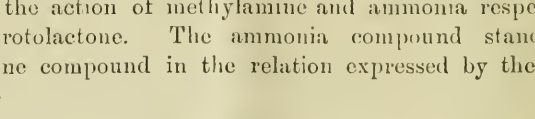
By distilling oxylepiden Zinin obtained from it a compound which he called *isolepiden*, assigning to it the formula $C_{28}H_{20}O$, whilst from the mother-liquors from this substance he obtained by the action of potash an acid of the formula $C_{28}H_{22}O_3$, to which he gave the name *isoxylepidenic acid*. The authors, therefore, following this analogy, distilled dibenzoylstyrolene, expecting to obtain from it isomerides of triphenylfurfuran and diphenylbenzoylpropionic acid respectively, but found that dibenzoylstyrolene was converted, with evolution of carbon monoxide, into a compound of the formula $C_{21}H_{16}O = C_{22}H_{16}O_2 - CO$, which formed lustrous, yellow crystals melting at 92—93°; whilst by the action of potash on the mother-liquors from this compound only ordinary diphenylbenzoylpropionic acid was obtained. As these results were in contradiction to the strict analogy elsewhere observable in the two sets of compounds, they repeated Zinin's experiment on the distillation of oxylepiden and found that the so-called isolepiden is formed, not by a process of deoxidation, as represented by Zinin, but with elimination of carbon monoxide: $C_{28}H_{20}O_2 = C_{27}H_{20}O + CO$, and is therefore not an isomeride of lepiden at all. The formulæ of the various hydro-"isolepidens" and oxy-"isolepidens" described by Zinin must also, therefore, be correspondingly modified.

From the mother-liquors from the compound $C_{27}H_{20}O$ the authors have obtained the so-called "isoxylepidenic acid," which proves, however, to be not isomeric, as stated by Zinin, but identical with oxylepidenic acid. The "acicular oxylepiden" is converted, during the heating, into "tabular oxylepiden," the greater part of which parts with carbonic oxide, forming "isolepiden," but a small portion distils unchanged and is hydrolysed in the subsequent treatment with alkali, yielding oxylepidenic acid. The analogy is, therefore, preserved also in this case.

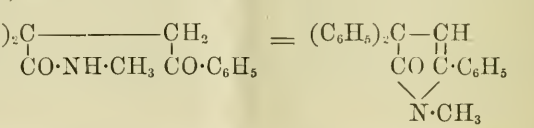
The remaining interactions of dibenzoylstyrolene described in this note have not yet been studied in the lepiden series.

By acting on dibenzoylstyrolene with ammonia the authors obtained (*Ber.*, **21**, 2936) two compounds of the formula $C_{22}H_{17}NO$: one melting at 180°, formed by mixing a warm solution of dibenzoylstyrolene with alcoholic ammonia; the second, melting at 221°, formed from the first by long boiling of its solutions, or by heating it alone. They now find that the various primary paraffinoid amines yield similar compounds. As yet only the compound formed with methylamine

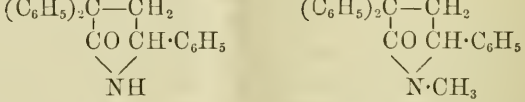
has been more fully investigated. This compound, which has the formula $C_{22}H_{16}(CH_3)NO$ and melts at 138—139°, and the ammonia compound $C_{22}H_{17}NO$, melting at 221°, can also be very readily obtained by the action of methylamine and ammonia respectively on triphenylcrotolactone. The ammonia compound stands to the methylamine compound in the relation expressed by the following formulæ—



Adopting a nomenclature based on that employed by Tafel (*Ber.*, **22**, 1861), these compounds would be called 3-*diphenyl*-5-*phenylpyrrholone* and 1-*methyl*-3-*diphenyl*-5-*phenylpyrrholone*; "pyrrholone" being equivalent to "ketopyrrholine," using "pyrrholine" in the generally accepted sense of "dihydropyrrhole." The latter compound may be obtained from triphenylcrotolactone and methylamine in two stages: in the first, the methylamide of diphenylbenzoylpropionic acid is formed; this, on heating, parts with water, yielding the compound $C_{22}H_{16}(CH_3)NO$—



On reduction with sodium and boiling amyl alcohol, these pyrrholones yield the corresponding dihydro-compounds or *pyrrholidones* —derivatives of tetrahydropyrrhole—

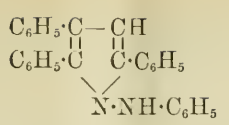


3-Diphenyl-5-phenyl-pyrrholidone (m. p. 201°).

1-Methyl-3-diphenyl-5-phenyl-pyrrholidone (m. p. 153·5°).

The pyrrholones in question also yield characteristic oxidation products and bromine-derivatives, which are still under investigation, as are also some remarkable cases of isomerism which the authors have discovered among the compounds formed by the action of alkylamines on dibenzoylstyrolene.

By the action of phenylhydrazine on dibenzoylstyrolene, Japp and Huntly obtained (Trans., 1888, 184) a compound of the formula $C_{28}H_{22}N_2$. The authors regard this as most probably an anilidotriphenylpyrrhole, of the constitution



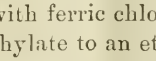
(*cf.* also Knorr, *Annalen*, **236**, 295). From the products of the same reaction they have isolated two further compounds: a substance $C_{28}H_{22}N_2O$ melting at 173—174°, which is apparently a monohydrazone of dibenzoylstyrolene; and a second compound, $C_{21}H_{16}N_2$, melting at 206°, formed by the action of the phenylhydrazine with elimination of a benzoyl-group from dibenzoylstyrolene; this appears to be a *triphenylpyrazole*, isomeric with Knorr and Laubmann's 1- 3- 5-triphenylpyrazole.

With hydroxylamine hydrochloride, dibenzoylstyrolene yields a compound $C_{15}H_{11}NO$, melting at 73—75°. Like the foregoing phenylhydrazine-derivative, with which it corresponds, it is formed with elimination of a benzoyl-group.

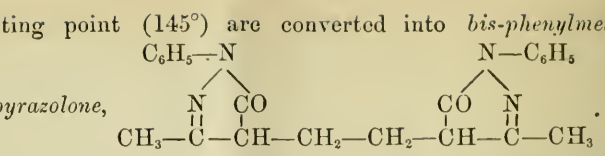
93. "Ethylic $\alpha\alpha_1$-diacetyladipate." By W. H. Perkin, jun., Ph.D.

Ethylene bromide and ethylic sodacetoacetate interact readily when heated together in alcoholic solution, forming ethylic acetyltrimethylenecarboxylate and ethylic $\alpha\alpha_1$-diacetyladipate,

These two substances may be readily separated by distillation in steam, the former passing over with the steam; the diacetyladipate may be extracted from the residue by ether, and is best purified by conversion into the crystalline diimido-compound, which is then hydrolysed by chlorhydric acid. Ethylic diacetyladipate is a thick, colourless oil, which gives with ferric chloride a fine violet coloration. On the addition of sodium ethylate to an ethereal solution, a yellowish-white precipitate of its disodium-derivative is produced, which is readily reconverted by acids into ethylic diacetyladipate.

Ethylic diimidodiacetyladipate,  separates from the solution of the ethereal salt in alcoholic ammonia in beautiful colourless plates, which melt at 170°. It readily dissolves in cold dilute acids, but on warming, decomposition into ethylic diacetyladipate and ammonia readily takes place. The corresponding *ethylic diphenylhydrazinediacetyladipate* is formed when ethylic diacetyladipate is warmed with excess of phenylhydrazine. It crystallises from alcohol in light yellow plates, which when heated above

their melting point (145°) are converted into *bis-phenylmethylmethylenepyrazolone*,



This substance crystallises from acetic acid in small prismatic needles, which do not melt at 250°. It is difficultly soluble in most of the ordinary solvents, but readily soluble in acids and alkalis.

When subjected to distillation under reduced pressure ethylic diacetyladipate yields a yellowish oily distillate, which appears to consist for the most part of three substances, all of which boil approximately at the same temperature (210—225° under 170 mm.), viz., *ethylic acetyladipate*, $\begin{matrix}CH_2\cdot CH_2\cdot CO_2Et\\ CH_2\cdot CH(Ac)CO_2Et\end{matrix}$; *ethylic methyldihydropentenemethylketonecarboxylate*, $CO_2Et\cdot CH<\begin{matrix}CH_2 — CH_2\\ C(CH_3):C\cdot Ac\end{matrix}$, and *ethylic methyldihydropentenedicarboxylate*, $CH_2<\begin{matrix}CH_2 —— CH\cdot CO_2Et\\ C(CO_2Et):C\cdot CH_3\end{matrix}$.

If the crude product of distillation be shaken with dilute aqueous potash, the ethylic acetyladipate dissolves, forming an acid ethereal salt, which, on distillation, is decomposed into carbon dioxide and ethylic ω-acetylvalerianate, a colourless oil boiling at 200—205° (150 mm.) *ω-Acetovalerianic acid*, which is readily obtained from the ethereal salt by hydrolysis, forms a crystalline mass which melts at 40—42°, and distils at 250—253° (280 mm.) with slight decomposition.

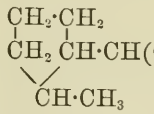
The residual oily product of distillation of ethylic diacetyladipate, which is insoluble in potassium hydrate, yields on hydrolysis two principal products. One of these is a neutral substance, $C_8H_{12}O$, which boils constantly at 191° and smells strongly of camphor. From its reactions this substance appears to be methyldihydropentenemethylketone, $CH_2<\begin{matrix}CH_2\cdot CH\cdot CO\cdot CH_3\\ CH_2\cdot C\cdot CH_3\end{matrix}$. It combines readily with hydroxylamine, forming a beautifully crystalline hydroxime, $C_8H_{13}NO$, which melts at 86°; when heated to 100° with Beckmann's reagent (acetic acid, acetic anhydride and hydrogen chloride) this compound is converted into an isomeric oily substance of pronounced basic properties, which boils at 164—165° and readily dissolves in water forming a strongly alkaline solution. The platinochloride $(C_8H_{13}NO)H_2PtCl_6$, crystallises from water in magnificent red prisms.

The second product of hydrolysis, methyldihydropentenedicarboxylic acid, crystallises from water in colourless plates which melt at 188°.

Concentrated sulphuric acid converts ethylic diacetyladipate into a substance of the formula $C_{12}H_{18}O_4$, which appears to be ethylic methyldihydropentene.

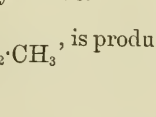
94. "(1·2) Methylethylpentamethylene." By T. Rhymer Marshall, D.Sc., and W. H. Perkin, jun., Ph.D.

Ethylic $\alpha\alpha_1$-diacetyladipate when carefully hydrolysed by alcoholic potash yields α-ω-diacetylbutane, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3$. This substance is a white, crystalline solid, which melts at 43—44°: it is converted by dehydrating agents, or by boiling with alcoholic potash, into the methyldehydropentenemethylketone described in the previous abstract.

Methylpentamethylenemethylcarbinol,  is obtained by reducing methyldihydropentenemethylketone with sodium in moist ethereal solution. It forms a colourless oil boiling at 181°, smelling strongly of menthol.

The *acetate*, $C_8H_{15}OC_2H_3O$, is readily prepared by boiling the alcohol with acetic anhydride. It boils at 133—135° (90 mm.), has a smell resembling that of the acetate of the higher alcohols of the fatty series, and is very readily hydrolysed by potash.

The *iodide*, $C_8H_{15}I$, is a colourless oil, boiling at 155—160° (90 mm.), which has an odour resembling that of amyliodide.

Methylethylpentamethylene,  , is produced when the iodide is heated with iodhydric acid and amorphous phosphorus in sealed tubes at 230—240° for eight hours. It is a limpid liquid boiling at 124° and smelling very like light petroleum. By the reduction of methyldihydropentenemethylketone with sodium in moist ether, a considerable quantity of a secondary product, $C_{16}H_{30}O_2$, is formed, which is a very thick oil boiling at 250—255° (50 mm.). If sodium amalgam be used as a reducing agent, two substances of complicated composition are formed, *i.e.*, $C_{16}H_{22}O$ (b. p. 220°, 25 mm. pressure) and $C_{16}H_{24}O_2$ (b. p. 250—260°, 25 mm. pressure).

95. "Action of dehydrating agents on α-ω-diacetylpentane. Formation of methylethylhexamethylene." By F. Stanley Kipping, Ph.D., D.Sc., and W. H. Perkin, jun., Ph.D.

α-ω-Diacetylpentane, under the influence of dehydrating agents,

loses one molecule of water and is converted into a compound of the formula $C_9H_{14}O$; although the constitution of this substance has not yet been proved beyond doubt, its formation and its properties seem to show that it has the constitution of an orthomethyltetrahydrobenzene methylketone (orthomethyacetyltetrahydrobenzene),

$$CH_2<\begin{matrix}CH_2\cdot CMe\\CH_2\cdot CH_2\end{matrix}>C\cdot COMe.$$

This compound is best prepared by dissolving diacetylpentane in concentrated sulphuric acid. It is a colourless, mobile oil, boiling at 205—206° and smelling strongly of peppermint; it is insoluble in water but is miscible with alcohol, ether, &c., in all proportions. It is not decomposed when heated with water at 150° or when treated with 80 per cent. sulphuric acid at the ordinary temperature; it does not combine with mercuric chloride.

The *hydroxime*, $C_6H_8Me\cdot CMe{:}NOH$, prepared by treating the ketone with hydroxylamine chlorhydride and excess of potash in alcoholic solution, is a thick, slightly yellow oil, sparingly soluble in hot water, readily in potash and concentrated hydrochloric acid. The *hydrazone*, $C_6H_8Me\cdot CMe{:}N_2Ph$, obtained by heating the ketone at 100° with phenlhydrazine, is a thick, yellow oil, which decomposes gradually on exposure to the air.

Orthomethylhexamethylenemethylcarbinol,

$$CH_2<\begin{matrix}CH_2\cdot CHMe\\CH_2-CH_2\end{matrix}>CH\cdot CHMe\cdot OH,$$

obtained by reducing methyltetrahydrobenzenemethylketone with sodium in moist ethereal solution, is a colourless oil, which boils at 195—200°, and has a smell very like that of menthol. It is insoluble in water, but is miscible with most of the ordinary solvents in all proportions, and it dissolves in concentrated hydriodic acid with evolution of heat.

The *acetate*, $C_6H_{10}Me\cdot CHMe\cdot OAc$, prepared by boiling the alcohol with acetic anhydride, is a colourless liquid boiling at 204—210°.

The *iodide*, $C_6H_{10}Me\cdot CHIMe$, is a heavy colourless liquid boiling at 178—180° (110 mm.) and possessing a smell exactly like that of amyl iodide.

Orthomethyltetrahydrobenzenemethylcarbinol,

$$CH_2<\begin{matrix}CH_2\cdot CMe\\CH_2\cdot CH_2\end{matrix}>C\cdot CHMe\cdot OH,$$

is formed in small quantities in the preparation of orthomethylhexamethylenemethylcarbinol when the quantity of sodium employed is insufficient for complete reduction. It is a colourless liquid boiling at 141—143° (50 mm.).

Orthomethylethylhexamethylene, $C_6H_{10}MeEt$, is obtained when methylhexamethylene methyl carbinol is heated at 230—240° for four hours with a large excess of hydriodic acid of sp. gr. 1·96 and a little amorphous phosphorus. It is a colourless mobile liquid, with a smell closely resembling that of light petroleum, and boils at 150—152°.

The compound $C_{18}H_{26}O$ is obtained in the preparation of diacetylpentane and is formed by the condensation of two molecules of the diketone with elimination of three molecules of water; it is a very thick yellowish oil boiling at 265—275° (35 mm).

A condensation compound, $C_{18}H_{32}O_2$, is formed in the reduction of methyltetrahydrobenzenemethylketone; it is a thick, yellowish oil, boiling at 255—265° (50 mm.).

96. "Action of reducing agents on α-ω-Diacetylpentane. Formation of Dimethylheptamethylene." By F. Stanley Kipping, Ph.D., D.Sc., and W. H. Perkin, jun., Ph.D.

When α-ω-diacetylpentane is treated with excess of sodium in moist ethereal solution, it is chiefly converted into orthodihydroxydimethylheptamethylene,

$$CH_2<\begin{matrix}CH_2\cdot CH_2\cdot CMe\cdot OH\\ CH_2\cdot CH_2\cdot CMe\cdot OH\end{matrix}$$

The same compound is formed when the diketone is reduced with sodium and alcohol at 80—100°. It is a thick, colourless liquid, with a sharp, bitter taste, and a peculiar aromatic smell, rather like that of menthol. It boils at 201—202° (180 mm.), is volatile with steam and distils, seemingly without decomposition, at the ordinary temperature when heated in small quantities. It is sparingly soluble in cold water, but separates from the solution on warming or on adding sodium carbonate. It does not combine with sodium hydrogen sulphite nor with hydroxylamine in alkaline solution. The sodium-derivative, $C_7H_{10}Me_2(OH)\cdot ONa$, seems to crystallise with $1\frac{1}{2}$ mols. H_2O, and is readily decomposed by water or when gently heated.

Orthodibromodimethylheptamethylene, $C_7H_{10}Br_2Me_2$, is obtained when the dihydroxy-compound is treated with excess of phosphoric bromide in chloroform solution. It is a yellowish mobile liquid, with an unpleasant, very irritating smell, and gradually decomposes on exposure to the air.

The *iodide*, $C_7H_{10}IMe_2\cdot OH$, can be prepared by boiling dihydroxydimethylheptamethylene with hydriodic acid of sp. gr. 1·96. It is a colourless oil, insoluble in water.

The diacetyl-derivative, $C_7H_{10}Me_2(OAc)_2$, prepared by boiling dihydroxydimethylheptamethylene with acetic anhydride, is a colour-

less mobile liquid, boiling at 199—202° (65 mm.); it is readily hydrolysed by potash.

Orthodimethylheptamethylene, $C_7H_{12}Me_2$, is obtained, together with considerable quantities of a condensation product, when dihydroxydimethylheptamethylene is heated at 230—250° for eight hours with a large excess of hydriodic acid of sp. gr. 1·96, and a little amorphous phosphorous. It is a colourless, mobile oil, boils at 150—152°, and has a smell not to be distinguished from that of light petroleum.

A compound, $C_{18}H_{34}O_3$, is formed in small quantities in the preparation of dihydroxydimethylheptamethylene; it is a very thick, yellowish oil, boiling at 300—310° (200 mm.).

97. "Oxyamidosulphonates and their conversion into Hyponitrites." By Edward Divers, M.D., F.R.S., and Tamemasa Haga, F.C.S.

The oxyamidosulphonates are the sulphazidates of Fremy, which Claus and Raschig have shown to be monosulphonic-derivatives of hydroxylamine. A modification of Fremy's method of preparing the acids has been devised by the authors, dependent on their discovery of the existence of a neutral soluble barium salt in addition to that of the basic salt. They find that the sodium salt can only be prepared as a colourless, very viscid liquid, which does not solidify in the desiccator. The potassium salt is crystalline, but is not anhydrous as stated by Claus.

The main interest of this paper lies in the behaviour of oxyamidosulphonates with strong alkalis, and with copper hydroxide. On treatment with alkali, instead of yielding sulphate and hydroxylamine, as asserted by Claus and Raschig: $HO{\cdot}NH{\cdot}SO_3K + KOH = HONH_2 + K_2SO_4$, and as it is admitted they do when hydrolysed by an acid, the authors find that they are converted exclusively into sulphite and hyponitrite, thus $2HO{\cdot}NH{\cdot}SO_3K + 4KOH = (KON)_2 + 2K_2SO_3 + 4OH_2$; this interaction affords much the most fruitful process known for converting nitrite into hyponitrite.

The reducing action of the sulphazidates was known even to Fremy, and has since been referred to the supposed conversion of the salts into hydroxylamine and sulphate, the hydroxylamine being supposed then to act on the copper hydroxide in the well-known way. The authors find in opposition to this belief that much sulphite as well as sulphate is formed, and that the cupric oxide reduced is only half that calculated on the above supposition. They would write the equation $2HO{\cdot}NH{\cdot}SO_3K + 2CuO + 2KOH = K_2SO_3 + K_2SO_4 + Cu_2O + N_2O + 3H_2O$, and hold that it is the undisplaced hydro-

of ammonia only which in the salt acts directly as the reducing agent.

. "The Alloys of Lead, Tin, Zinc and Cadmium." By A. P. Laurie.

In extension of his previous observations (*Trans.*, 1888, p. 88) the author has made voltaic cells with the various alloys and has thus compared their behaviour with that of the single metal by means of an electrometer. He concludes that the metals now examined do not combine together, thus confirming Matthiessen's conclusions.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Zur Erinnerung an vorangegangene Freunde. Gesammelte Gedächtnissreden, von A. W. Hofmann. Drei Bände. Braunschweig 1888. From the Author.

Principles of Chemistry, by D. Mendeléeff. St. Petersburg 1889. (In Russian.) From the Author.

The Microscope in the Brewery and Malt-house, by C. G. Matthews and F. E. Lott. London 1889. From the Authors.

The Clinical Use of Prisms and the Decentering of Lenses, by E. E. Maddox. Bristol and London 1889. From the Author.

Ausführliches Lehrbuch der Chemie, von H. E. Roscoe und C. Schorlemmer. Zweiter Band: Die Metalle und Spectralanalyse. Zweite vermehrte Auflage. Braunschweig 1889. Vierter Band: Die Kohlenwassertoffe und ihre Derivate oder Organische Chemie, Zweiter Theil; Vierte Abtheilung. Braunschweig 1889. From the Authors.

Service Chemistry, being a Short Manual of Chemistry and its Applications in the Naval and Military Services, by V. B. Lewes. London 1889. From the Author.

Ammonia and Ammonium Compounds; a practical Manual for Manufacturers, Chemists, Gas Engineers, and Drysalters, by R. Arnold. Translated from the German by H. G. Colman. London 1889. From the Publishers.

Watt's Manual of Chemistry. Vol. 1. Physical and Inorganic Chemistry. Second edition (14th edition of Fownes) by W. A. Tilden. London 1889. From the Publishers.

Chemical Technology, or Chemistry in its Applications to Arts and Manufacturers, edited by C. E. Groves and W. Thorp. Vol. 1.

Fuel and its Applications by E. J. Mills and F. J. Rowan. London 1889. From the Publishers.

A Text-Book of Organic Chemistry, by A. Bernthsen. Translated by G. M'Gowan. London 1889. From the Translator.

Lehrbuch der Stöchiometrie und der allgemeinen theoretischen Chemie, von C. F. Rammelsberg. Berlin 1842.
From Dr. J. H. Gladstone, F.R.S.

Chemie der organischen Verbindungen, von C. Löwig. Zweite Auflage. 2 Bände. Braunschweig 1846.
From Dr. J. H. Gladstone, F.R.S.

Gaseous Fuel, by B. H. Thwaite. London 1889.
From the Author.

Ueber Capillar-Analyse, und ihre verschiedene Anwendungen sowie über das Emporsteigen der Farbstoffe in den Pflanzen mit Beilage. Von F. Goppelsroeder. Wien 1889. From the Author.

Farbelectrochemische Mittheilungen, von F. Goppelsroeder. Mülhausen 1889. From the Author.

Practical Photometry: a Guide to the Study of the Measurement of Light, by W. J. Dibdin. London 1889. From the Author.

Offensive Trades, by S. A. Goldschmidt. New York 1889.
From the Author.

Catalogue of the Transactions of Societies, Periodicals, and Memoirs in the Reading Room of the Radcliffe Library at the Oxford Museum. Oxford 1887. From the Librarian

Coloured Analytical Tables, by H. Wilson Hake. London 1889.
From the Author.

At the next meeting, on Thursday, November 21st, the following paper will be read:—

"The law of the freezing points of solutions." By S. U. Pickering, M.A.

HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY, ST. MARTIN'S LANE.

Issued 28/11/1889.

ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 73. Session 1889–90.

November 21st, 1889. Dr. W. J. Russell, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. James Munro Taylor Anderson, Edgar House, Combs, Suffolk; George Frederick Brindley, Aluminium Company, Oldbury, near Birmingham; Philip Howard Davis, 106, Talcott Road, S.W.; Alexander Charles Farquharson, 13, Stonebyres Terrace, Partick, Glasgow; P. J. Hartog, 6, Greville Road, London, N.W.; Robert Law, 70, Maxwell Road, Pollokshields, Glasgow; Hugh Marshall, 1, Lorne Terrace, Edinburgh; Francis Herbert Mason, Outalpa, Harlesden, N.W.; Edgar Philip Penman, B.Sc., 32, Oakington Road, Elgin Avenue, W.; Edward Russell, 75, Kelvin Road, Highbury Park, N.; Henry Heron Smith, Wilton House, Vicarage Park, Plumstead, S.E.; John Wade, 129, High Road, Lee, S.E.

The following papers were read:—

99. "The law of the freezing points of Solutions." By S. U. Pickering.

Although the influence which a substance exerts in lowering the freezing point of a solvent, when used with caution, may give valuable evidence as to its molecular weight in the quasi-gaseous condition, it is impossible to accept Raoult's statement of the observed facts as a general law of freezing points. The so-called constant exhibits a variation of some 20 or 30 per cent. in the case of different substances (not counting those cases where the values are admittedly abnormal), and may also vary to the same, or to a greater, extent, when different proportions of the same substance and solvent are taken, even when

we confine our attention to cases where the proportion is that of not more than 1 mol. to 100 mols. of the solvent. Still less can we, on the strength of the supposed constancy of the value, draw any conclusions from it respecting the nature of solutions.

The author believes that he has found the law which regulates the freezing point of a solution of any strength. He attributes the lowering produced by the dissolved substance to three distinct causes, which he classifies as (1) mechanical, (2) physical, and (3) chemical.

In the first place he points out that if a weak solution (taking water as a concrete instance of a solvent) consists, as he maintains it does, of a hydrate, the water which crystallises out on cooling is derived from the hydrate itself: which is thermally possible, since the heat of solidification of the water is far in excess of the heat of formation of the hydrate. Hence the whole hydrate does not act as the "foreign molecule," but only that part of it which is not water, *e.g.*, H_2SO_4; and hence, also, the molecular weight obtained by Raoult's method is that of the H_2SO_4 and not that of the hydrate. But, although the decomposition of a complex hydrate into the next lower one and solid water is an exothermic change, such would not be the case with all the lower hydrates, and, in fact, the limit of possible decomposition is fixed very clearly at the hydrate containing $5{\cdot}5H_2O$. In the same way the limits of the two branches of each of the curves representing the crystallisation of $H_2SO_4{\cdot}4H_2O$ and $H_2SO_4{\cdot}H_2O$, and that of the one branch of the H_2SO_4 curve, can be established from thermochemical considerations, and all these limits agree very well with the nature of the curves obtained experimentally.

(1.) *Mechanical Lowering.*—Considering the foreign molecules to be uniformly distributed throughout the solvent, and considering, also, for the sake of simplicity, that the molecules are stationary, the author argues that the solvent molecules will be entirely isolated from each other, and, therefore, will be prevented from combining to form the aggregates of which a solid is constituted, when there are 300 foreign molecules to every 100 molecules of the solvent. This value obtains only if we consider the molecules on a superficies, but the author argues on experimental as well as general grounds that crystallisation is entirely a surface action. The temperature below which a liquid will not solidify is $-160°$, according to Person (see Trans., 1889, 32): hence 300 foreign molecules to the 100 will lower the freezing point of water 160°, and one molecule will lower it by $(160 \div 300 =)\ 0{\cdot}53°$, a constant closely approximating to that ($0{\cdot}63°$) found by Raoult for various solvents freezing at about the same temperature as water. In the case of water, Raoult's work shows that the active molecule is not H_2O but $3H_2O$; the mechanical constant will, therefore, be $(\cdot57 \times 3 =)\ 1{\cdot}6°$.

(2.) *Physical Lowering.*—If water be superfused to $t°$ below its normal freezing point, and, then be made to crystallise, the heat evolved in its solidification diminishes regularly with the value for $t°$ from 1430 cal. per H_2O at 0° to *nil* at −160°; if $t°$ be −79°, or any lower temperature, the whole of the water will solidify, whereas for smaller values of t, the amount solidifying is given by $\frac{t}{79}$, and the heat evolved in this partial solidification will always be exactly sufficient to raise the resulting mixture of ice and water from $t°$ to 0°. If, however, we take a hydrate, say, $H_2SO_4 13H_2O$, the freezing point (water crystallising out) of which is −34°, the total water available for crystallisation is only $7{\cdot}5H_2O$, for no amount of cold would suffice to decompose the residual hydrate $H_2SO_4 5{\cdot}5H_2O$; the amount of water which would crystallise would, therefore, be $\frac{34}{79}$ of $7{\cdot}5H_2O$, or $3{\cdot}2124H_2O$, and the heat evolved in its crystallisation is easily calculated, being 3615 cal. After the crystallisation a mixture of $3{\cdot}2124H_2O$ as ice, $(7{\cdot}5-3{\cdot}2124)H_2O$ as water and $H_2SO_4 5{\cdot}5H_2O$ would remain, the total heat capacity of which is 223·5, and this mixture would be raised 16·17° by the 3615 cal. evolved, instead of 34° as would have been the case had there been nothing but the water present. The freezing point, therefore, will have been lowered (34°−16·17° =) 17·83° from this "physical" cause.

(3.) *Chemical Lowering.*—A definite hydrate such as $H_2SO_4 13H_2O$ can only give up its water by decomposing into the next lower hydrate, $H_2SO_4 9H_2O$ in the instance taken: the heat absorbed in this change is given by the heat of dissolution curve (863 cal.), and will lower the temperature of a mixture with a heat capacity of 223·5 cal. by 3·5°.

The sum of these three lowerings gives −33·64° as the freezing point, whereas −34·0° is the value obtained. The former is more strictly a calculated verification of the observed value than a calculated value; but it is in calculating the physical lowering only that the observed value is taken to start with, and the author finds that if a wrong value be taken for the freezing point the "calculated" value does not agree with it, and that by a series of approximations we might ultimately obtain the true value starting with any temperature in the first instance. The following instances may be quoted:—

Hydrate.	Per cent. H_2SO_4.	F. p. found.	F. p. calculated.
$H_2SO_4,130H_2O$....	4·02	−1·59	−1·39
„ 60 „	8·59	−3·80	−3·44
„ 24 „	18·49	−11·83	−11·52
„ 13 „	29·53	−34·00	−33·64
„ 9 „	37·70	−72·63	−72·77

After the hydrate with $13H_2O$, the active water-molecule becomes simplified, attaining the formula H_2O before the hydrate with $9H_2O$ is reached. A similar simplification has been observed at about the same molecular composition in the case of mixtures of alcohol and water. Instead of calculating the freezing point, we may take the observed freezing point and calculate the heat evolved in the chemical action, and, hence, the composition of the next lower hydrate formed in the reaction. The values given by the last three of the above-mentioned freezing points are—

Position of next hydrate		Found,	29·5	p. c.	Calc.,	31·1	p. c.
,,	,,	,,	37·7	,,	,,	38·5	,,
,,	,,	,,	49·8	,,	,,	49·5	,,

In the other two cases the chemical lowering is so small in comparison with the errors inherent in the calculations, that the calculated position of the next hydrate is valueless.

If no definite hydrates existed in solution, the chemical lowering would be absent; its absence would always increase the discrepancy between the observed and calculated values, and in the last three cases would destroy all semblance of agreement, the differences amounting to from 1·6° to 10·3°.

In the case of very weak solutions (0·36 and 0·37 per cent.), the actual error between the observed and calculated values is less than 0·01°, but this is a relatively large quantity, and is probably due to errors in the experimental method adopted. A very striking confirmation of the composition of the hydrates at these points may, however, be obtained by comparing the figures representing the found and calculated values. Very definite proof is thus obtained that the author was wrong in supposing the existence of a hydrate with $510H_2O$ (1·0 per cent.), but right as to the others.

The correctness of the calculated values affords proof not only of the position of the next hydrate, but also of there being a hydrate of the composition of the solution at which the f. p. is taken. Points intermediate between definite hydrates may be correctly calculated on the supposition that the liquid consists of a mixture of next higher and next lower hydrate; whereas, if the calculation be based on the wrong supposition that the liquid consists of one definite hydrate, wrong values are obtained; thus:—

$H_2SO_4 16H_2O$ = 25·4 p. c.: the f. p. found was −23·0°; that calculated for a mixture of $H_2SO_4 24H_2O$ and $H_2SO_4 13H_2O$ is −22·36°; that calculated for a definite hydrate is −20·75°.

Very strong evidence of the existence of certain definite hydrates may be deduced from the limit assigned on thermochemical grounds

($H_2SO_4 5{\cdot}5H_2O$) to the decomposition of the hydrates. Thus, taking the f. p. of the solution $H_2SO_4 13H_2O$, we get $-34°$ as the found value, and $-33{\cdot}64$ as the value calculated with the above-mentioned limit; whereas, if the limit be taken to be the next hydrate above or below that with $5{\cdot}5H_2O$, namely, those with 9 and $4H_2O$, we get $-41{\cdot}51$ and $-30{\cdot}18$ as the calculated values respectively: and, more important still, if we take that limit which would hold good on the physical theory of there being no definite hydrates in solution, which limit would be at about $H_2SO_4 7H_2O$, we get $-37{\cdot}11°$ instead of $-34°$ as the calculated value.

The results obtained in calculating the lowering of the freezing point of sulphuric acid by the addition of water do not, from several causes, agree so well with the observed values as in the case of the water curve; but the differences are not great, and, though they prevent the correct calculation of the composition of the hydrates present, they are not sufficient to prevent our drawing from them further important confirmation of the general truth of the author's theory, and of concluding that the active molecules are, in this case, H_2SO_4 and H_2O respectively. The results mentioned are the following:—

$36H_2SO_4H_2O$,	99·49	p. c.	F. p. found.		$-3{\cdot}05°$	F. p. calc..		$-1{\cdot}89°$
12	,,	98·49	,,	,,	,,	$-8{\cdot}85$	,,	,,	$-7{\cdot}38$
6	,,	97·03	,,	,,	,,	$-18{\cdot}60$	,,	,,	$-16{\cdot}97$
3	,,	94·23	,,	,,	,,	$-41{\cdot}60$	,,	,,	$-38{\cdot}61$

these numbers representing degrees below the f. p. of the pure acid (10·35° C.).

In the case of the crystallisation of the monohydrate, the active molecule of sulphuric acid appears to be $12H_2SO_4$ throughout; while on the other branch of the curve where the f. p. is lowered by the addition of water, the "mechanical lowering" appears to be absent. This is probably due to the active molecule of water being very complex; if it were 12 times as big as it is when *it* is the crystallising substance (*i.e.*, the same proportion which obtains in the case of the sulphuric acid molecules), it would be $36H_2O$, and the lowering thereby produced would be practically negligible. The magnitude of the active molecules of the "foreign substance" in this case is probably due to the fact that the crystallising substance actually contains some of each of them, and therefore exerts less influence on them than would otherwise be the case. The fact that we have to determine the magnitude of the mechanical constant in the first instance from the curve does not detract much from the value of the deductions as to the calculated values; for one point is sufficient to give us the

value of the constant, and we can then apply it in an indefinite number of other points. The instances given are—

Hydrate.	P. c.	F. p. found.	F. p. calculated.	Next hydrate.	
				Found.	Calculated.
				p. c.	p. c.
$H_2SO_4H_2O,\frac{1}{0}H_2SO_4$...	86·40	−2·2	−2·36	89·10	88·46
,, $\frac{1}{2}$,, ...	89·10	−9·8	−10·14	94·23	93·65
,, 2 ,, ...	94·23	(−60·7)	−63·19	—	—
,, $\frac{1}{6}$ H_2O....	82·36	−2·10	−2·13	78·41	78·45
,, $\frac{1}{2}$,, ...	78·41	−15·41	−15·05	73·14	72·78

Of the 20 hydrates which the author has already announced as existing in the case of sulphuric acid, one has been definitely disproved by the present calculations; in the case of three others the evidence is insufficient to be termed proof; while proof of the most definite description is obtained in the case of the remaining. The hydrate $H_2SO_4 4H_2O$ is included, since the mere existence of the curve representing its crystallisation is ample proof of its existence, though there are no data existing in this case at present on which to found any calculations of the freezing points.

Discussion.

Professor Ramsay said that it was impossible without careful study to offer any valuable criticism on so comprehensive a paper, opening up such new points of view. He drew attention to the fact that the supporters of Van't Hoff's theory of the existence of a substance dissolved in a liquid in a molecular state comparable with that of a gas by no means shut their eyes to the possibility, and in many cases the probability, of the existence of complex molecules, either of the solvent itself, or of compounds of the solvents with the dissolved substance. He also questioned the correctness of Person's data on which it was assumed that the "solid-liquid critical point" was −160°, inasmuch as it is founded on insufficient data regarding the specific heats of solids and liquids at low temperatures. With reference to the sudden change in the molecular complexity of the water-molecule, assumed by Mr. Pickering to occur between the hydrate with $13H_2O$ and that with $9H_2O$, he suggested that a gradual disruption of the complex water-molecule would be more likely, and stated that from experiments of his own it appeared more probable that the water-molecule consists of $4H_2O$. The existence of complex molecules of

sulphuric acid he regarded as supported by the fact of there being double sulphates of such formulæ as $NaH_7(SO_4)_4$.

Mr. Pickering, in reply, said that it was quite true that Person's "absolute zero" of −160° was more or less hypothetical. But it was founded on considerations precisely analogous to those on which the "absolute zero" for gases, −273°, was founded; and, just as the latter, though hypothetical also, yields correct results in all cases where true gases are concerned, so the former yields correct results in the case of liquids. He pointed out that the change of the acting water-molecule from $3H_2O$ to H_2O was not sudden, but was spread over a range 8 per cent. in the strength of the solutions. There were no signs of the change beginning before the solutions attained the composition $H_2SO_413H_2O$. Finally, although, according to Raoult's work, the active molecule of water in this and in the majority of cases appeared to be $3H_2O$, there were other instances in which it attained the magnitude $4H_2O$.

100. "The constituents of Flax." By C. F. Cross and E. J. Bevan.

The authors describe the results of their examination of the cuticular constituents of the fibre, the only investigation of which hitherto published is that of F. Hodges (*Proc. R. Irish Acad.*, 1881, **3**, 460). On exhaustion with boiling alcohol, the fibre loses 3—4 per cent. of its weight; as the solution cools it deposits a greenish-white resin, which on hydrolysis with alcoholic soda yields a wax alcohol, identified as ceryl alcohol. In addition to the alcohol an oily, ketone-like substance was obtained. The residue appeared to be unresolved: on submitting it to drastic treatment with alkalis, two fatty acids were obtained, one of which, from its equivalent and melting point, appears to be cerotic acid. A considerable residue of unresolved products remained.

The green filtrate from the resin-wax yielded on distillation a green, oily residue. From this a further quantity (10 per cent.) of ceryl alcohol was isolated, and a much larger proportion of the oily ketone (15 per cent); the residue being a complex of ill-defined, inert compounds, yielding "ketones" on hydrolysis. These "ketones" have the characteristic odour of raw flax and flax goods, and from their property of emulsifying with water, no doubt exercise an important influence on the wet processes of fine spinning of flax.

The pectic group of constituents associated with the cellulose in the fibre proper was found to yield mucic acid on oxidation with nitric acid ($d = 1{\cdot}15$).

The isolation of a pure cellulose from flax is a difficult operation. The presence of unremoved cuticular constituents accounts for the statements of Godeffroy, that flax cellulose reduces silver nitrate when boiled with a neutral solution of the salt, pure flax cellulose resembling cotton cellulose in resisting the action of this agent. Flax cellulose oxidised with permanganate in alkaline solution yields, in addition to oxycellulose and oxalic acid, acid bodies, from which furfural is obtained by acid hydrolysis.

101. "Acetylcarbinol (Acetol), $CH_3{\cdot}CO{\cdot}CH_2{\cdot}OH$." (Preliminary notice.) By W. H. Perkin, Jun., and J. Bishop Tingle, Ph.D.

This important substance, the first member of the series of ketone alcohols, has never been isolated, although its dilute aqueous solution has repeatedly been obtained. The authors have succeeded in preparing it in an anhydrous condition by the following method:—25 grams of monochloracetone is slowly added from a dropping funnel to 200 c.c. of water containing an excess of freshly precipitated barium carbonate in suspension, the whole being vigorously boiled during the operation. As soon as the monochloracetone has dissolved, and the evolution of carbon dioxide has practically ceased, the liquid is filtered, and the resulting, almost colourless solution is distilled. The distillate is now treated with chloracetone and barium carbonate and again distilled, the operation being repeated until 150 grams of chloracetone have been treated. The resulting moderately concentrated solution of acetylcarbinol is saturated with potassium carbonate, and extracted at least 50 times with pure ether. The ethereal solution is thoroughly dried by means of ignited potassium carbonate, and is then slowly evaporated; a colourless oil remains, the greater part of which passed over on distillation between 140° and 150°. On refractioning, a considerable quantity was obtained boiling at 145—150°, which gave on analysis numbers agreeing with the formula $CH_3{\cdot}CO{\cdot}CH_2{\cdot}OH$, viz., C = 48·73 and H = 8·33, instead of C = 48·65 and H = 8·11.

Two vapour-density determinations by Hofmann's method in xylene vapour gave d = 35 and 34, instead of 37.

Acetylcarbinol is a colourless oil, possessing a faint and peculiar odour, and a sweet but burning taste. It is miscible with water, and very readily reduces Fehling's solution in the cold.

When heated with excess of phenylhydrazine, it is converted into its osazone, $\begin{matrix} CH_3{\cdot}C{:}N_2HC_6H_5 \\ | \\ CH{:}NH_2C_6H_5 \end{matrix}$, which melts at 145°. This substance has already been prepared by Laubmann (*Annalen*, **243**,

p. 244), and is identical with the compound obtained by Pechmann (*Ber.*, **20**, 2543) from methylglyoxal and nitrosoacetone.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Repetittorium der Chemie; mit besonderer Berücksichtigung der für die Medicin wichtigen Verbindungen, von C. Arnold. Dritte Aufl. Hamburg and Leipzig 1889. From the Publisher.

An Introduction to Chemical Science, by R. P. Williams, edited and revised by B. P. Lascelles. London 1889. From the Publishers.

U.S. Department of Agriculture. Bulletin, No. 13, Food and Food Adulterants: Part 5th, Baking Powders, by C. A. Crampton. No. 22, Record of Experiments at Des Lignes Sugar Experiment Station, by C. A. Crampton. No. 23, Record of Experiments at the Sugar Experiment Station on Calumet Plantation, by H. Edson. Washington 1889. From the Department.

Sur la Polarisation rotatoire du Chlorate de Soude, par C. E. Guye. Genève 1889. (Pamphlet.) From the Author.

Department of Mines, Sydney. Records of the Geological Survey of New South Wales. Vol. I. Part II. Sydney 1889. From the Department.

Outbursts of Gas in Metalliferous Mines, by B. H. Brough. Newcastle-on-Tyne 1889. (Pamphlet.) From the Author.

The History of a Field newly laid down to Permanent Grass, by Sir J. B. Lawes. London 1889. (Pamphlet.) From the Author.

Report on the Chemistry Department at the People's Palace, East London, by A. P. Laurie. 1889. (Pamphlet.) From the Author.

II. *By Purchase.*

Travaux et Mémoires du Bureau international des Poids et Mesures. Tome VI. Paris 1888.

Das Furfuran und seine Derivate, von A. Bender. Berlin 1889.

Anleitung zur chemisch-technischen Analyse organischer Stoffe, von F. M. Horn. Wien 1889.

Das Chinolin und seine Derivate, von A. Reissert. Braunschweig, 1889.

Handbuch der Mineralogie von C. Hintze. Lief. I. Leipzig 1889.

Lehrbuch der physiologischen und pathologischen Chemie, von G. Bunge. Leipzig 1889.

Die synthetischen Darstellungsmethoden der Kohlenstoff-Verbindungen, von K. Elbs. Erster Band. Leipzig 1889.

Vollständiges Handbuch der galvanischen Metall-Niederschläge, von G. Langbein. Leipzig 1889.

Die Farben-Industrie (Vierteljahresbericht), von E. Börnstein. Heft I. Oct.—Dec., 1888. Berlin 1889.

Les plantes médicinales indigènes et exotiques, leurs usages thérapeutiques, pharmaceutiques, et industriels, par Dujardin-Beaumetz et E. Égasse. Paris 1889.

Die Technik der Rosanilinfarbstoffe, von O. Mühlhäuser. Stuttgart 1889.

HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY, ST. MARTIN'S LANE.

Issued 11/12/1889.

ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 74. Session 1889–90.

December 5th, 1889. Dr. W. J. Russell, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. Frederick Graham Ansell, Wickwar, Gloucester; Sydney Hoare Collins, 19, Riverdale Road, Stoke Newington, N.; John B. Coppock, 126, Walton Street, Brompton, S.W.; Thomas Southall Dymond, 37, Hart Street, Bloomsbury; Cuthbert Chapman Gibbes, 3, Wyburn Villas, Surbiton; James Grant, Belmont Place, Chadderton, Oldham; Joseph H. Heywood, 23, Holland Street, Rochdale; James Guthrie Mactaggart, Eskbank, Eltham, S.E.; James Sibun, 2, Lax Terrace, Norton, Stockton-on-Tees; Henry Wood Smith, B.Sc., Belmont, Higher Broughton, Manchester; John Stokes, Sarum House, Park Gate, Rotherham, Yorks; James Walker, 8, Windsor Terrace, Dundee; Sydney Russell Wells, 14, Girdlers Road, West Kensington.

The following were duly elected Fellows of the Society:—Messrs. Frank Thornton Addyman, Charles Frederic Baker, B.Sc., John Burgess, William Frederic Butcher, Frank Hill Perry Coste, David Brown Dott, Thomas William Dukes, Robert Stephen Edwards, B.A., James Kerr Erskine, John Simpson Ford, John Foggie, Harold Gripper, H. B. Helbing, Robert Edward Hughes, Eric Henry Jackson, James Robert Kaye, Henry Richard Kenwood, Frederick Thomas Knott, L. Napier Ledingham, G. B. Mason, James Braik Mason, Thomas Mercer, Joseph Alfred Nettleton, Wallace Christopher Nickels, J. T. Norman, James Gordon Parker, Alfred Edridge Pike, William Ping, Frederick Quincke, Ph.D., Sydney Steel, Sidney Augustus Sworn, John Bishop Tingle, Willis G. Tucker, M.D., Daniel Walker, B.Sc., William Whitehouse, Matthew Whittam, Basil P. Wigan, John Wiltshire, John Wilkie.

The following papers were read:—

102. "Compounds of phenanthraquinone with metallic salts." By Francis R. Japp, F.R.S., and Alfred E. Turner.

The authors have obtained several double compounds of phenanthraquinone with metallic salts, viz., $C_{14}H_8O_2{\cdot}ZnCl_2$, which forms dark reddish-brown needles, not melting even above 300°; $(C_{14}H_8O_2)_2HgCl_2$, crystallising in red, obliquely truncated prisms, melting at 222—223°; and $(C_{14}H_8O_2)_2HgCy_2$, which also forms red crystals, melting like the foregoing, at 222—223°. Oxysalts do not unite with phenanthraquinone.

They have prepared a similar compound (not analysed) from mercuric chloride and β-naphthaquinone; but could not obtain double compounds from benzoquinone, α-naphthaquinone, anthraquinone, diacetyl and benzil. It would therefore appear that compounds of this class are derivable only from orthoquinones, and not from paraquinones, or open-chain α-diketones.

The intense colour of the double compounds in question indicates that in them the quinone preserves its distinctive character. In this respect they differ from the colourless compounds of the orthoquinones with hydrogen sodium sulphite, the formation of which involves a reduction, and which are to be regarded as quinol-derivatives.

Discussion.

Dr. Armstrong remarked that the preparation and study of compounds such as the authors described was of importance in elucidating the nature of molecular compounds, and as affording valuable material for the discussion of the problem of valency. It was highly remarkable that the compounds were so much more intensely coloured than phenanthraquinone. Were their solutions equally coloured, and did the colour vary much with the concentration; would it not be possible by observation of the colour of solutions of varying strength to determine to what extent the compounds existed in solution, and at the same time to apply to them the Raoult freezing point method?

Dr. Japp, in reply, said that the intense colour of the compound was at once apparent on mixing hot solutions of zinc chloride and of phenanthraquinone in glacial acetic acid, but the compound immediately began to separate out; it was so sparingly soluble that it would not be possible to determine the molecular weight by Raoult's method. In preparing the mercury compounds acetone was used as solvent; like the zinc compound they were decomposed by water and also by acetic acid.

Mr. Chapman said that on mixing solutions of dextrose and of nickel

oxide in ammonia, a dark green liquid was obtained of the colour of the compound, which subsequently crystallised out.

103. "Action of aldehydes and ammonia on α-diketones." By G. H. Wadsworth, Associate of the Normal School of Science.

The author has studied the action of various aldehydes and ammonia on diacetyl, and has obtained the following glyoxalines:—

With benzaldehyde: *phenyldimethylglyoxaline*, $C_{11}H_{12}N_2$; slender needles, melting at 230—234°.

With salicylaldehyde: *o-hydroxyphenyldimethylglyoxaline*, $C_{11}H_{12}N_2O$; satiny needles, melting at 218°.

With cinnamic aldehyde: *cinnamenyldimethylglyoxaline*, $C_{13}H_{14}N_2$; warty crystals, melting at 201—202°.

In addition, *cinnamenyldiphenyleneoxazole*, $C_{23}H_{15}NO$, has been prepared by the action of cinnamic aldehyde and ammonia on phenanthraquinone; slender yellow needles, melting at 171—172°.

104. "Phenylhexamethylene derivatives." By F. Stanley Kipping, Ph.D., D.Sc., and W. H. Perkin, jun., Ph.D.

The authors find that on boiling phenyldehydrohexonecarboxylic acid, $C_6H_5\cdot C=C\cdot COOH$ / $O<$ ___ $>CH_2$, $CH_2\cdot CH_2$, with water it yields benzoylbutyl alcohol, $C_6H_5\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$, and carbon dioxide. This alcohol crystallises from water in large, flat plates which melt at 40—41°: although stable under ordinary conditions, when placed over sulphuric acid, the crystals rapidly disappear and are converted into oily drops of phenyldehydrohexone.

The *hydroxime*, $C_6H_5\cdot C(N\cdot OH)\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$, is readily obtained by the interaction of benzoylbutyl alcohol, hydroxylamine hydrochloride and excess of potash in alcoholic solution. It crystallises from benzene in colourless, microscopic plates which melt at 56—57°.

Phenylpentylene glycol, $C_6H_5\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$, prepared by the action of an excess of sodium amalgam on a dilute alcoholic solution of benzoylbutyl alcohol, crystallises from benzene in colourless, concentrically grouped needles which melt at 54°; it is readily soluble in ether, alcohol, benzene and hot water, but only sparingly in light petroleum.

Phenylpentylene dibromide, $C_6H_5\cdot CHBr\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2Br$, is best prepared by dissolving the glycol in chloroform and gradually adding a slight excess of phosphorus pentabromide; it is a slightly brownish-coloured, disagreeably-smelling oil which is insoluble in

water. It is readily acted upon by ethylic sodiomalonate, forming ethylic phenylhexamethylenedicarboxylate, $\begin{matrix}CH_2\cdot CH_2\cdot CH\cdot C_6H_5\\ CH_2\cdot CH_2\cdot C(CO_2Et)_2\end{matrix}$. By heating the oily acid obtained from this ethereal salt at 180—200°, *phenylhexamethylene monocarboxylic acid*, $\begin{matrix}CH_2\cdot CH_2\cdot CH\cdot C_6H_5\\ CH_2\cdot CH_2\cdot CH\cdot COOH\end{matrix}$, is produced. This acid is best purified by conversion first into the barium salt and then into the crystalline ammonium salt. It crystallises from light petroleum in short, thick prisms which melt at 104—105°; it is readily soluble in ether, alcohol, chloroform and acetone, only moderately easily in cold light petroleum, difficultly soluble in water.

On boiling an alcoholic solution of phenylpentylene dibromide and ethylic sodacetoacetate the two substances readily interact, yielding ethylic acetylphenylhexamethylenecarboxylate,

$$\begin{matrix}CH_2\cdot CH_2\cdot CH\cdot C_6H_5\\ CH_2\cdot CH_2\cdot C(CO\cdot CH_3)\cdot COOC_2H_5\end{matrix}.$$

On hydrolysis this ethereal salt yields phenylhexamethylenecarboxylic acid (m. p. 104—105), identical with the acid described above, and *phenylhexamethylenemethylketone*, $\begin{matrix}CH_2\cdot CH_2\cdot CH\cdot C_6H_5\\ CH_2\cdot CH_2\cdot CH\cdot CO\cdot CH_3\end{matrix}$. This substance crystallises in colourless needles, melting at 78—79°, and distils at about 187—190° under 40 mm. pressure without decomposition: the hydroxime produced by treating it with hydroxylamine and excess of potash in alcoholic solution is a thick, colourless oil, which could not be obtained in a crystalline condition.

105. "Diphenylfurfuran." By W. H. Perkin, jun., Ph.D., and Aug. Schloesser, Ph.D., M.Sc.

Ethylic dibenzoylsuccinate, $\begin{matrix}C_6H_5\cdot CO\cdot CH\cdot CO_2Et\\ C_6H_5\cdot CO\cdot CH\cdot CO_2Et\end{matrix}$, is best prepared by treating an ethereal solution of ethylic benzoylacetate with the calculated quantity of sodium (1 atomic proportion) in the form of fine wire and then adding a slight excess of iodine. It is converted by concentrated sulphuric acid into ethylic diphenylfurfurandicarboxylate, $O<\begin{matrix}C_6H_5\cdot C=C\cdot CO_2Et\\ C_6H_5\cdot C=C\cdot CO_2Et\end{matrix}$; on hydrolysis, it yields the dicarboxylic acid.

Diphenylfurfuranmonocarboxylic acid, $O<\begin{matrix}C_6H_5\cdot C=CH\\ C_6H_5\cdot C=C\cdot COOH\end{matrix}$, is obtained, together with diphenylfurfuran, on heating the dicarb-

oxylic acid at about 250°. It crystallises from benzene in short, colourless needles which melt at about 214°. It does not yield a hydroxime when treated with hydroxylamine, neither is it affected by boiling with acetic anhydride.

Diphenylfurfuranmonocarboxylic acid tetrabromide, $C_{17}H_{12}Br_4O_3$, is produced when the finely-divided acid is exposed to the vapour of bromine as a hard, crystalline mass, almost insoluble in solvents.

Diphenylfurfuran, $\begin{matrix} & C_6H_5\cdot C{=}CH \\ O< & \quad\quad | \\ & C_6H_5\cdot C{=}CH \end{matrix}$, crystallises from light petroleum in pearly plates which melt at 81° and distil at a high temperature almost without decomposition. It is very readily soluble in benzene and alcohol, but sparingly soluble in cold, light petroleum.

Diphenylfurfuran tetrabromide, $C_{16}H_{12}Br_4O$. This compound is readily produced when diphenylfurfuran is exposed for some hours to the action of bromine-vapour. The resulting dark-coloured mass becomes almost colourless when placed over caustic potash; when purified by recrystallisation from benzene, it forms beautiful satiny plates melting at 190°.

Oktohydrodiphenylfurfuran, $C_{16}H_{20}O$, is produced when a boiling alcoholic solution of diphenylfurfuran is treated with an excess of sodium. It is a slightly yellowish-coloured oil which boils at 150—155° under 110 mm. pressure.

ADDITIONS TO LIBRARY.

I. *Donations.*

Georg Agricola's Mineralogische Schriften, übersetzt von E. Lehmann. Vier Bände. Freyberg 1806–12.

From Hy. Bassett, Esq.

A General System of Chemical Knowledge, and its Application to the Phenomena of Nature and Art, by A. F. Fourcroy; translated from the original French by W. Nicholson. Ten vols. London 1804.

From Hy. Bassett, Esq.

Elementary Lectures on Chemistry and Natural History, by A. F. Fourcroy; translated by T. Elliott. Two vols. Edinburgh 1785.

From Hy. Bassett, Esq.

Aus Justus Liebig's und Friedrich Wöhler's Briefwechsel in den Jahren 1829—73; unter Mitwirkung von Emile Wöhler, herausgegeben von A. W. Hofmann. Zwei Bände. Braunschweig 1888.

From Sir H. E. Roscoe, F.R.S.

II. *By Purchase.*

The Chemistry of Photography, by R. Meldola. London 1889.

The Rothamsted Experiments on the Growth of Wheat, Barley, and the Mixed Herbage of Grass Land, by W. Fream. London 1888.

A Text-Book of Paper-Making, by C. E. Cross and E. J. Bevan. London 1888.

A Text-Book of Physiology, by M. Foster. Parts I and II. London 1888–9.

Practical Metallurgy and Assaying, by A. H. Hiorns. London 1888.

Index of Spectra, by W. M. Watts. Revised and Enlarged Edition. Manchester 1889.

Alcaloïdes: histoire, propriétés chimiques et physiques, extraction, action physiologique, effets thérapeutiques, toxicologie, observations, usages en médecine, formules &c., par B. Dupuy; avec préface de Dujardin-Beaumetz. Deux tomes. Paris 1888.

Das Pyridin und seine nächsten Derivate, von M. Philip. Stuttgart 1889.

Agriculturchemische Analyse, von E. Wein. Stuttgart 1889.

The Chemical Analysis of Iron; a complete account of all the best known methods, by A. A. Blair. Philadelphia 1888.

At the next meeting, on December 19th, the following paper will be read:—

"On Frangulin." By Prof. Thorpe, F.R.S., and H. H. Robinson, M.A.

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ABSTRACTS OF THE PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 75. Session 1889–90.

December 19th, 1889. Dr. W. J. Russell, F.R.S., President, in the Chair.

Messrs. W. F. Butcher, C. F. Baker, A. L. MacLeroy and F. Quincke were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Edward Whitley Allsom, Palace View, Cork; William Winson Haldane Gee, B.Sc., 124, Raby Street, Moss Lane East, Manchester; Arthur Hutchinson, Christ's College, Cambridge; Arthur Hotham McConnell, 10/2, Russell Chambers, Bury Street, W.C.; William Samuel Newman, Madras, India; Saville Shaw, Durham College of Science, Newcastle; William Charles Sayers, 63, High Street, Lewisham, S.E.

The following papers were read:—

106. "Frangulin." By Professor T. E. Thorpe, F.R.S., and H. H. Robinson, M.A.

The authors prepared the glucoside frangulin from the bark of the alder buckthorn (*Rhamnus frangula*) by first extracting with low boiling petroleum to remove plant fat, and next with methylated spirit, which removed the frangulin together with resins, &c. To this extract lead acetate was added to precipitate tannins, and after removing the excess of lead in the filtrate by means of sulphuretted hydrogen, the frangulin was obtained from it. 14 lbs. of the bark gave about $5\frac{1}{2}$ grams of frangulin.

Seven analyses were made of four different portions of frangulin which had been purified by different methods, and the results agreed

with one another and corresponded to the formula $C_{22}H_{22}O_9$: for every analysis the frangulin was dried at 120° until constant.

The frangulin was hydrolysed and the yellow product insoluble in water was analysed, in two cases after crystallising from alcohol and drying at 120° until constant, and in two cases after crystallising from benzene and drying at 180°. The results corresponded to the formula $C_{15}H_{10}O_5$. The product was directly compared with some emodin from rhubarb, and was found to give the same colour reactions, and the authors are satisfied as to its identity with that substance.

A phenylhydrazine-derivative of the product soluble in water, and which has the power of reducing Fehling's solution, was prepared and compared with that obtained from glucose, and was found to possess quite different properties: hence it is concluded that the soluble product of the hydrolysis is not glucose.

The investigation of the nature of this soluble product, and of the equation representing the hydrolysis, will be continued by one of the authors.

107. "Arabinon, the saccharon of arabinose." By C. O. Sullivan, F.R.S.

In a former communication (*cf. Chem. Soc. Trans.*, 1884, p. 55), under the name of α-arabinose, the author has described a substance obtained by hydrolysis of arabic acid, having an optical activity "well above $[\alpha]_j = 140$"; this is more fully considered in the present communication. The details of its preparation from geddic acid, an acid obtained from Gedda gum—which the author will describe in a future notice—are fully given. As yet it has not been obtained in a crystalline state: when dried over sulphuric acid in vacuo, and then at a temperature gradually increasing to 75—80°, it is obtained as a glassy mass, which when pulverised forms a white hygroscopic powder. It has a specific rotatory power of $[\alpha]_D = 198{\cdot}8°$; and 100 parts have the same cupric reducing-power as 58·8 parts of dextrose. It yields arabinose on hydrolysis, and appears to bear a similar relation to this carbohydrate that saccharon (cane-sugar) bears to glucose: the author therefore terms it *arabinon*, preferring the vowel system of nomenclature to that proposed by Scheibler. Combustions were simultaneously made of saccharon and arabinon with the following results:—

	Saccharon.	Arabinon.	Theory for $C_{10}H_{15}O_9$.
Carbon.....	42·11	42·46	42·58
Hydrogen....	6·61	6·55	6·38

The molecular weight found by Raoult's method was 239·2; that of a carbohydrate of the formula $C_{10}H_{18}O_9$ is 282, and although the number obtained is low, bearing in mind the fact that this is the case with the "on" carbohydrates, and that the preparation may not have been free from ash constituents, there can be no doubt that the compound belongs to the "on" and not to the "in" or dextrin class. The amount of arabinose obtained on hydrolysing 100 parts arabinon was 104·9; the theoretical yield if $C_{10}H_{18}O_9 + H_2O = 2C_5H_{10}O_5$ is 106·3.

108, "On the identity of cerebrose and galactose." By Horace T. Brown, F.R.S., and G. Harris Morris, Ph.D.

The authors give the results of an examination of a sample of *cerebrose* prepared from phrenosin, which was placed in their hands early in 1888 by Dr. Thudichum, who first isolated and crystallised this substance. They show that its specific rotatory power, cupric reducing power, and molecular weight as determined by Raoult's method, are identical with those of *galactose*, thus confirming the recent work of Thierfelder (*Zeit. physiol. Chem.*, **14**, 209), who has proved the sugar produced by the action of acid on cerebrin to be galactose.

Discussion.

Dr. Thudichum said that the specimen of cerebrose which has been examined by the author was prepared by him from *phrenosin*, $C_{41}H_{79}NO_8$. Messrs. Brown and Morris's experiments had been conducted in July, 1888, and Mr. Brown's communication to him (Dr. Thudichum) on the subject, which he held in his hand, was dated August, 1888. Phrenosin consisted of the sugar now shown to be identical with galactose, $C_6H_{12}O_6$; of *neurostearic acid*, $C_{18}H_{36}O_2$, an isomer of stearic acid, fusing at 84°; and of *sphingosin*, an alkaloid of the formula $C_{17}H_{35}NO_2$. There were, however, present in the brain a number of glucosides or saccharides of which phrenosin was the most abundant and most characteristic; amongst the more neutral bodies of this kind was *kerasin*, $C_{42}H_{55}NO_8$, and amongst the more acid ones, which formed insoluble compounds with baryta or lead oxide, were three—cerebrinic acid, spherocerebrinic acid, and the principal (in quantity) cerebrinacide, compounds containing from 54 to 59 atoms of carbon and from 9 to 21 atoms of oxygen. Of these, cerebrinic acid had also yielded the sugar; the others had not yet been tested in that respect. The compounds of this group present in the human brain were very numerous, and one of them contained as much as 4 per cent. of sulphur in organic combination. Some human brains contained

as much as 4 per cent. of phrenosin, and therefore a human brain of 1,500 grams in weight contained potentially 15 grams of galactose. In some diseases of a neurotic type he had found "cerebrose" in the urine, and of the cases of glycosuria of nervous origin so-called a certain proportion was no doubt due to the decomposition of some phrenosin in the brain and the consequent passage of the "cerebrose" into the circulation and out of it by way of the renal emanatories. It was an important fact that the crystallised sugar from phrenosin was always accompanied by an almost equal weight of uncrystallisable sugar of which the nature was not yet ascertained. Mr. Brown believed that his (Dr. Thudichum's) crystallised galactose, made from pure phrenosin, contained a little dextrose: the question then arose, whether the uncrystallised sugar obtained was altered galactose or dextrose, or a sugar *sui generis;* if it was dextrose, or a sugar *sui generis*, the formula of phrenosin would have to be doubled, and it must be assumed to contain an *amylonide radicle*, such as he in his theory of the organoplastic substances had considered as forming the chemical skeleton of the albuminous matters. The special details concerning the substance alluded to were to be found in his "Treatise on the Chemical Constitution of the Brain," London, 1884, and an exhaustive critical consideration of the literature and chemistry of the "cerebrosides" or cerebrin bodies of the brain was contained in his German work on "Anatomical and Clinical Chemistry," Berlin, 1886.

109. "The action of chloroform and alcoholic potash on hydrazines." Part III. By S. Ruhemann, Ph.D., M.A.

The products formed by the interaction of these substances are to be regarded as derivatives of *tetrazine*, $N\lessdot^{CH\cdot NH}_{NH\cdot CH}\gtrdot N$ (*cf. Chem. Soc. Trans.*, 1889, 242). The author describes the di-paratolyl, orthotolyl and pseudocumyl derivatives, and their behaviour with nitric acid and bromine.

Paraditolyltetrazine is a weaker base than the diphenyl homologue; it forms an unstable monochlorhydride and a monomethiodide.

The ortho-compound appears to be somewhat more basic. It is noteworthy that while the formation of tetrazines from phenyl- and paratolyl-hydrazine is accompanied by that of the formylhydrazine, the formyl-derivative is not produced in the case of orthotolyl-hydrazine, although it is easily obtained by the interaction of the hydrazine and formamide.

Incidentally, the author describes pseudocumylhydrazine and several of its derivatives.

Mr. P. Braham exhibited a spectroscope without a lens, which was described at the meeting of the British Association at Newcastle. It consists of a taper tube, with a slit at one end and a direct vision prism at the other.

ADDITIONS TO LIBRARY.

I. *Donations.*

A System of Chemistry, by T. Thomson. Third Edition. Five vols. Edinburgh, 1807.

Polygraphices: *Liber septimus;* of Alchymie, wherein is treated of the true Philosopher's Tincture and Process of the same: *Liber octavus;* Faber's Arcanum, translated from the Latin by W. Salmon: *Liber nonus;* of Chiromantical Signatures: *Liber decimus;* of Painting and Colouring, or Staining Glass, Enamel and Gems: *Liber undecimus;* of Varnishing, Japanning, and Gilding. London (No title page or date).

Conversations on Chemistry, by Mrs. Marcet. Two vols. London 1807.

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From the Author.

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PROCEEDINGS

OF

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DATES OF ISSUE OF THE MONTHLY NUMBERS OF THE JOURNAL OF THE CHEMICAL SOCIETY TO FELLOWS.

January number	was issued	9th January.
February	,,	4th February.
March	,,	19th March.
April	,,	12th April.
May	,,	12th May.
June	,,	13th June.
July	,,	9th July.
August	,,	9th August.
September	,,	6th September.
October	,,	11th October.
November	,,	8th November.
December	,,	19th December.
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£15 to Dr. F. S. Kipping for the synthesis of heptamethylene derivatives.

£25 to Messrs. Cross and Bevan for the further prosecution of their experiments on the nature of cellulose.

£10 to Mr. E. A. Werner for the study of thiocarbamide derivatives.

£10 to Messrs. Linder and Picton for the continuation of their experiments on hydrosulphides.

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Abrines, Gustavus A.	November 6th	December 4th.
Allsom, Edward W.	December 19th, 1889.	February 6th.
Anderson, Frederic A.	January 16th	March 6th.
Anderson, James M. T.	November 21st, 1889.	February 6th.
Ansell, Frederick G.	December 5th, 1889.	„ „
Appleyard, James R.	April 3rd	May 15th.
Babington, Percival	February 6th	March 6th.
Bamber, M. K.	November 6th	December 4th.
Barker, Joseph	March 6th	April 17th.
Beardmore, G. R.	January 16th	March 6th.
Beck, Charles R.	March 6th	April 17th.
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Blake, Robert F.	January 16th	„ „
Blake, William H.	April 3rd	May 15th.
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Blount, Bertram	January 16th	March 6th.
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Brierley, John T.	November 6th	December 4th.
Brindley, George F.	November 21st, 1889.	February 6th.
Brownsword, Frank	November 6th	December 4th.
Butcher, William J.	„ „	„ „
Butler, William W.	„ „	„ „
Bunting, Henry H.	January 16th	March 6th.
Burton, William	February 6th	„ „
Cheetham, Thomas A.	November 6th	December 4th.
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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 76. Session 1889–90.

January 16th, 1890. Dr. W. J. Russell, F.R.S., President, in the Chair.

Messrs. Wallace C. Nickels and J. A. Nettleton were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Frederick Alfred Anderson, B.Sc., Lesney House, Erith, Kent; G. Russell Beardmore, Warwick House, Upper Street, Islington; Robert Frederick Blake, 37, Hartington Street, Dublin Road, Belfast; Bertram Blount, Laboratory, Broadway, Westminster; Henry Herbert Bunting, 82, Netherwood Road, Kensington, W.; Paul Alexander Cobbold, Warwick School, Warwick; John S. Lumsden, 5, Paradise Road, Dundee; Frederick Mills, Bevan Crescent, Stockton-on-Tees; Robert Richard Rothwell, 82, Mawson Street, Ardwick Green, Manchester; Edward Sergeant, 75, Park Road, Bolton; Basil William Valentin, Aston Brewery, Birmingham.

The following papers were read:—

1. "A new method of estimating the oxygen dissolved in water." By J. C. Thresh, D.Sc., M.B.

The process is based on the observation that whereas, in absence of oxygen, nitrous acid and hydrogen iodide interact to form iodine, water and nitric oxide; in presence of oxygen the nitric oxide becomes re-oxidised, and, serving as a carrier of the oxygen, an amount of iodine equivalent to the oxygen present is liberated, in addition to that resulting from the initial action of the nitrous acid: hence, deducting the amount liberated by the nitrous acid and by the oxygen

dissolved in the solutions used from the total amount, the difference will be that corresponding to the oxygen dissolved in the water examined.

The solutions used are: (1) a solution containing ·5 gram sodium nitrite and 20 grams potassium iodide in 100 c.c.; (2) a solution of 7·75 grams sodium thiosulphate in 1 litre, 1 c.c. of which corresponds to 0·25 milligram of oxygen; (3) a clear solution of starch; and (4) diluted pure sulphuric acid (1 : 3).

The apparatus required is a very simple one. It consists of a wide-mouth, white glass bottle of about 500 c.c. capacity, provided with a caoutchouc stopper, through which four holes are bored. Through one passes the neck of a cylindrical "separator" funnel of known capacity, and through the second a tube drawn out to a fine point, which is connected by a short length of caoutchouc tubing with the thiosulphate burette; while inlet and exit tubes for coal gas are passed through the third and fourth holes, the exit tube having attached to it a sufficient length of caoutchouc tubing to permit of connexion being established between the bottle and the separator when the stopper of the latter is withdrawn.

The separator is filled with the water to be examined, and 1 c.c. of the nitrite-iodide and 1 c.c. of the acid solution are added; if the pipette be held vertically, with its end just below the surface of the water, the solutions flow in a sharply defined column to the lower part of the separator, so that an infinitesimally small quantity (if any) is lost in the water which overflows when the stopper is inserted. The admixture of the liquids having been effected by inverting the apparatus several times, a sharp current of coal gas is passed into the bottle to displace the air, the escaping gas being allowed to burn at a jet attached to the exit tube. Fifteen minutes after adding the solutions to the water the flame is extinguished, a cork is attached in place of the jet and is inserted in place of the stopper of the separator, and the water is then allowed to flow into the bottle; the exit tube having been disconnected from the funnel and the gas set fire to. thiosulphate is run in until the colour of the iodine is nearly destroyed; about 1 c.c. of starch is then added from the separator and the titration is completed. The effect of the nitrite, dilute acid and starch solutions is readily determined by removing the separator and adding 5 c.c. of each in succession and then titrating; the effect of the oxygen in the thiosulphate may be allowed for on the assumption that as much oxygen is dissolved in it as distilled water would contain at the same temperature. It appears that there is no advantage in passing the coal gas through alkaline pyrogallol.

The author states that concordant results are easily obtained, and that the results in the case of freshly distilled water closely agree

with those recently published by Sir Henry Roscoe and Mr. Lunt (*cf. Chem. Soc. Proc.*, 1889, 124 ; *Trans.*, 1889, 552). Thus :—

Temp.	Thresh.	Roscoe and Lunt.
10°	7·81	7·77
15	7·02	6·96
20	6·17	6·22
25	5·69	5·60
30	5·45	5·43

Discussion.

Mr. Warington said that on the occasion of Mr. Holland having suggested in the *Chemical News* a method of estimating nitrites in water by means of potassium iodide, he had pointed out that the method was fallacious in presence of air; the delicacy of the iodine test for nitrites was doubtless ascribable to the occurrence of the series of changes of which Dr. Thresh had availed himself.

Mr. Green stated that he also had called attention to the influence of oxygen about four years ago, in a communication to the University College Chemical Society.

Dr. Stevenson said that he was not satisfied with the method of estimating nitrites in water proposed by the author; a comparison with other methods would be desirable.

Mr. Chapman Jones drew attention to the use of manganous hydrate in estimating the oxygen dissolved in water.

2. "Note on a milk of abnormal quality." By F. J. Lloyd.

The author is led to give the results of his examination of the milk afforded by two cross-bred shorthorns, as its quality appears to be altogether remarkable (compare table); there being no evidence either that the cows were suffering from disease, or that they were insufficiently or improperly fed, he is of opinion that the normal quality of their milk is such as has never before been recorded. Several complete analyses, made with the object of discovering whether the loss fell on any special constituent, show that this is not the case, the caseine, sugar and other constituents, except the mineral matters, being equally affected.

Discussion.

Dr. Stevenson expressed the opinion that the animals in question were in some way suffering from malnutrition, or were subject to some latent disease.

Mr. Warington said that the amount of total solids was not below

Composition of the Milk.

Yield of milk.		Date.	No. 40.						No. 41.					
			Morning.			Evening.			Morning.			Evening.		
40	41		Fat.	Other solids.	Total solids.	Fat.	Other solids.	Total solids.	Fat.	Other solids.	Total solids.	Fat.	Other solids.	Total solids.
38 lbs.	37 lbs.	13th Nov.	3·41	8·47	11·88	5·71	8·63	14·34	—	—	—	—	—	—
—	—	19th „	—	—	—	—	—	—	3·80	8·24	12·04	4·54	8·10	12·64
—	—	22nd „	3·39	8·39	11·78	4·50	8·38	12·88	3·80	8·38	12·18	4·61	8·41	13·02
22 „	25 „	5th Dec.	3·44	8·28	11·72	5·12	8·48	13·60	3·07	8·21	11·28	4·50	8·52	13·02
—	—	10th „	2·17	7·87	10·04	4·68	8·30	12·98	3·13	8·19	11·32	5·13	8·25	13·38
15 „	22 „	17th „	2·98	7·58	10·56	3·86	8·14	12·00	3·27	8·27	11·54	4·26	8·26	12·52
8 „	18 „	7th Jan.	2·70	7·50	10·20	3·64	7·68	11·32	3·93	8·13	12·06	4·95	8·19	13·14

the accepted lowest value; whilst Professor KINCH remarked that equally low results had been obtained in certain cases at the Agricultural College, Cirencester.

Professor THOMSON mentioned the case of a cow having the propensity of eating heather tops affording a milk containing a lower proportion of total solids than that of other cows of the herd which had not the propensity.

Mr. LLOYD, in reply, said that in the cases considered by him the small amount of solids other than fat was what he desired to bring under notice; the total solids often varied, but the variation was chiefly in the amount of fat, not in the solids other than fat.

3. "The sulphates of antimony." By R. H. Adie, B.A.

Having previously studied the compounds of arsenious oxide with SO_3, the author has now examined those of antimonious oxide. His results are summarised in the following table, in which is indicated the composition of the products obtained from the two oxides on treatment with the acid formulated in the first column.

SO_3	$As_2O_3,8SO_3$	$Sb_2O_3,9SO_3$
$2H_2SO_4,SO_3$	$As_2O_3,4SO_3$	$Sb_2O_3,4SO_3$
H_2SO_4	$As_2O_3,2SO_3$	$Sb_2O_3,3SO_3$ or $Sb_2(SO_4)_3$
$9H_2SO_4,3H_2O$ to H_2SO_4,H_2O	As_2O_3,SO_3	
$H_2SO_4,2H_2O$	—	$Sb_2O_3,2SO_3,H_2O$ or $Sb(OH)SO_4$
$H_2SO_4,4H_2O$	—	$Sb_2O_3,2SO_3,3H_2O$ or $Sb(OH)SO_4,H_2O$
Action on sulphate of alcohol..	—	$Sb_2O_3,2SO_3$ or $SbO(SO_4)_2$
Cold water	As_2O_3	$2Sb_2O_3,SO_3$, $x$aq.
Hot water	—	$7Sb_2O_3,2SO_3,y$aq.

Where $x = 4$ to 16 and $y = 2$ to 16.

On comparing the two series of compounds it appears that:—

(i.) With H_2SO_4 and weaker acids, Sb_2O_3 forms a different order of sulphates from As_2O_3, while it resembles it in forming acid sulphates when subjected to the action of stronger acids. Thus the former yields the characteristic group salt, $Sb_2(SO_4)_3$, in place of the basic $As_2O(SO_4)_2$ afforded by the latter. The limits of existence, both as regards dilution and temperature, are much narrower for the arsenic than for the antimony salt. The practically complete formation of $Sb_2(SO_4)_3$ in one crystallisation also contrasts with the formation of $As_2O(SO_4)_2$ only by repeated crystallisation.

(ii.) Arsenious oxide does not form any basic sulphates containing water, while the more metallic antimonious oxide does form hydrated sulphates in acids weaker than H_2SO_4,H_2O. This acid is the limit of existence of $Sb_2(SO_4)_3$ in solution, and of any arsenic sulphate whatever.

At the meeting on March 20th, Professor Judd, F.R.S., will deliver a lecture on *the evidence afforded by petrographical research of the occurrence of chemical change under great pressures.*

At the next meeting, on February 6th, there will be a ballot for the election of Fellows, and the following papers will be read :—

"The oxides of nitrogen." By Professor Ramsay, F.R.S.

"Studies on the constitution of tri-derivatives of naphthalene." By Dr. Armstrong and W. P. Wynne.

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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 77. Session 1889–90.

February 6th, 1890. Dr. W. J. Russell, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. Percival Babington, Elmfield, Rotherham, Yorks; Richard Berncastel, 38, Ventnor Villas, Brighton; William Burton, 18, Victoria Street, Basford, Stoke-on-Trent; John Dennant, Lyndhurst Crescent, Glenferrie, Melbourne; Frank Gosling, Waldegrave Road, Teddington; John Charles Jackson, 51, Wellington Road, St. John's Wood, N.W.; Alfred E. Macintyre, Saint John, N.B., Canada; Ira Moore, Sutton Crosshills *viâ* Keighley; John Myles, Butterburn Park, Hamilton.

The following were elected Fellows of the Society:—

Edward Whitley Allsom, James Munro Taylor Anderson, Frederick Graham Ansell, George Frederick Brindley, Sydney Hoare Collins, John B. Coppock, Thomas Southall Dymond, Alexander Charles Farquharson, Cuthbert Chapman Gibbes, James Grant, William Winson Haldane Gee, B.Sc., P. J. Hartog, Joseph H. Heywood, Arthur Hutchinson, Robert Law, James Guthrie Mactaggart, Arthur Hotham McConnell, Hugh Marshall, Francis Herbert Mason, William Samuel Newman, Edgar Philip Perman, B.Sc., Edward Russell, William Charles Sayers, Saville Shaw, Harry Wood Smith, B.Sc., Henry Heron Smith, John Stokes, John Wade, James Walker, Sydney Russell Wells, B.Sc.

The following papers were read:—

4. "Observations on nitrous anhydride and nitrogen peroxide." By Professor Ramsay, Ph.D., F.R.S.

The author recommends as the best method of preparing pure nitrogen peroxide that the deep blue-green liquid, supposed to be

a mixture of this oxide and nitrous anhydride, which is obtained by condensing the products of the interaction of arsenious oxide and nitric acid, be added to a solution of nitric anhydride in nitric and phosphoric acids, prepared by adding phosphoric anhydride to well cooled nitric acid; after agitating the mixture, the upper layer is decanted and distilled. He assumes that the two oxides interact thus: $N_2O_5 + N_2O_3 = N_2O_4$.

The melting point of the peroxide was found to be 10·14°, in agreement with Deville and Troost's statement. The depression in the freezing point caused by one part of chloroform in 100 parts of the peroxide was 0·35°, and by one part of chlorobenzene 0·37°: the molecular depression is therefore 41.

The heat of fusion (W) of the peroxide, calculated from this number and the observed fusing point, by Van't Hoff's formula $W = \frac{0{\cdot}02T^2}{t}$, where T is the freezing point of the solvent in absolute degreos and t the molecular depression, is 33·7 cals.; a direct determination gave 32·3.

To determine the molecular weight of nitrous anhydride, a known weight of nitric oxide was passed into the peroxide and the depression of the freezing point determined; assuming that an amount of nitrous anhydride equivalent to the nitric oxide was formed, the results gave the values 80·9, 92·7 and 81·0, instead of 74, the value corresponding to the formula N_2O_3. The author was unsuccessful in freezing nitrous anhydride even at −90° by means of liquefied nitrous oxide. It was found to be soluble in this liquid, and it was further observed that as evaporation took place nitric oxide gas was given off together with the nitrous oxide: it would therefore appear that N_2O_3 is unstable, even at the very low temperature at which nitrous oxide is liquid.

Discussion.

Referring to Professor Ramsay's determination of the heat of fusion of nitrogen peroxide, Mr. Pickering said that observations on substances which exercise an appreciable influence on each other cannot be safely used in deducing the heat of fusion. Thus, in the case of mixtures of water and sulphuric acid, solutions containing 29·5, 18·5, 8·6, 1·0 and 0·07 per cent. of acid gave respectively the values 37·4, 58·3, 79·9, 74·9 and 56·3 as the heat of fusion of water, instead of 79·6. In strong solutions the lowering of the freezing point is always abnormally great; in such solutions, according to the theory of osmotic pressure, the dissolved molecules, being more subject to each other's attraction, should exercise less attraction on the mole-

cules of the solvent, and these latter, therefore, should coalesce more readily to form a solid.

Mr. Groves remarked that sulphuric acid might be used in preference to phosphoric anhydride in preparing pure nitrogen peroxide: the liquid product obtained by warming arsenious oxide with a mixture of two parts nitric and one of sulphuric acid might be freed from the small proportion of nitrous anhydride which it contained by treatment with sulphuric and a little nitric acid, and on then distilling, pure nitrogen peroxide was obtained.

Mr. Wynne inquired whether Professor Ramsay had examined the action of nitric oxide on nitric anhydride: it had been stated that the interaction was between N_2O_3 and N_2O_5, but nitric oxide alone should have the same effect.

Professor Ramsay, in reply, said that the method of preparing nitrogen peroxide described by Mr. Groves gave good results, but was less economical than his own. He had not examined the action of nitric oxide on nitric anhydride.

5. "Note on the law of the freezing points of solutions." By S. U. Pickering.

According to views explained in a previous communication (these Proceedings, 1889), the author considers the lowering of the freezing point of a solvent to be attributable to three actions, which he distinguishes as mechanical, physical and chemical. He has now succeeded in reducing the values for these actions into one equation which gives the total lowering of the the freezing point, $t°$, to be

$$t° = \frac{K + 167 \pm \sqrt{(K - 167)^2 - 668\,\frac{Kl + H}{Ac}}}{2},$$

where l is the heat capacity of the limiting hydrate (that is, the hydrate from which no amount of cooling could make water crystallise out); H the heat absorbed in the decomposition of the hydrate (or hydrates) constituting the solution taken into the next lower one; A the maximum number of water molecules which could be crystallised out by excessive cooling; C the heat capacity of water. The author applies a small correction to Person's so-called absolute zero, −160°, based on a combination of Person's with Regnault's values for the heat capacity of ice, and gets −167°, a value which he finds gives results in his calculations of the freezing points agreeing with those found even more closely than −160° did. K represents the "mechanical" lowering, this being equal to $\frac{n167m}{300}$ in which n is the

number of foreign (fundamental) molecules (of sulphuric acid in the case taken) to 100 H_2O, and m the number of fundamental molecules constituting the active molecule of the solvent; in the case of water, m is generally 3.

In his former communication the author stated that the triple molecules of water began to simplify when sulphuric acid solutions of 30 per cent. strength were reached, being resolved into simple or H_2O molecules when the strength reached about 38 per cent. The above equation shows that this simplification must occur. As the strength of the solution increases, K becomes bigger, and a point is reached where the value of $668\frac{Kl + H}{Ac}$ is bigger than $(K - 167)^2$, so that the contents of the surd are negative, and there will be no freezing point possible under these conditions. This occurs at 34 per cent.: and the only way in which water could be frozen out of solutions of greater strength (as is the case) is by the reduction of the magnitude of K by the simplification of the $3H_2O$ molecules, that is, by the reduction of the value for m.

Proceeding with this reduced value for K, another point (37·95 per cent.) is soon reached where the freezing out of water would become impossible, even under these new conditions, and, as the H_2O molecules could simplify no further, it must cease absolutely; as a matter of fact it does so: the crystallisation of water ceasing at about 38·2 per cent., while that of the tetrahydrate begins.

6. "The action of chromium oxychloride on nitrobenzene." By G. G. Henderson, B.Sc., M.A., and J. M. Campbell, B.Sc.

These substances interact, suddenly, and with great violence, even at the ordinary temperature, and no definite products are obtained. When a 50 per cent. solution of chromium oxychloride in dry chloroform is heated on the water-bath with a similar solution of nitrobenzene, hydrogen chloride is evolved and a brown powder slowly separates. After it has been washed with chloroform and dried, this powder has the composition $C_6H_3(NO_2)2CrO_2Cl$: it rapidly takes up moisture, and when thrown into water is decomposed with evolution of much heat, chromic chloride and chromic acid going into solution and nitrobenzene separating out, but the authors have failed to obtain the nitroquinone described by Étard. On using nitrobenzene containing nitrotoluene it was found, however, that a brown compound was produced which, when decomposed by water, gave nitrobenzene and, in smaller quantity, paranitrobenzoic acid; the latter substance has properties very similar to those attributed to nitroquinone, and it is suggested that Étard may have mistaken one for the other.

7. "Studies on the constitution of the tri-derivatives of naphthalene. No. 1. The constitution of betanaphthol- and betanaphthylaminedisulphonic acids R and G. Naphthalenemetadisulphonic acid." By Henry E. Armstrong and W. P. Wynne.

The study of the tri-derivatives of naphthalene is of importance from many points of view, both technical and theoretical; several are largely used in the preparation of azo-dyes, and it is necessary that their constitution should be known in order that the dependence of colour and tinctorial properties on structure may be determined; and especially is this the case, as all are not equally valuable—betanaphtholdisulphonic acid G (Gelb), like the "Bayer" modification of betanaphtholmonosulphonic acid, interacting but slowly with diazo-salts; while the corresponding betanaphthylaminedisulphonic acid, like the "Badische" modification of betanaphthylaminemonosulphonic acid, is incapable of forming azo-dyes with the majority of diazo-salts.

Moreover, having characterised all the dichloronaphthalenes by converting them into sulphonic acids, the authors were anxious also to determine the exact course of the change on sulphonation, especially as isomeric changes were noticed in several instances (*cf.* these Proceedings, 1889, 52, 120), it being probable that much light would thus be thrown on the laws which govern substitution in the naphthalene series; and from this same point of view, the comparative study of the influence exercised by radicles such as Cl, OH and NH_2 on the formation of disulphonic acids appeared likely to afford results of considerable interest.

In the case of the dichloronaphthalenes, which serve as reference compounds for di-derivatives of naphthalene, the authors' previous work has shown how much is to be learnt by carefully characterising the several isomerides (*cf.* these Proceedings, 1888, 104); and in the case of the trichloronaphthalenes, no fewer than fourteen of which are possible, which will ultimately serve as reference compounds for tri-derivatives of naphthalene, it is still more necessary to characterise each compound, owing to the close similarity which obtains between many of the isomerides: no fewer than four, for example, melt at nearly the same temperature, about 90—92°.

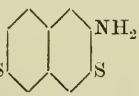
The study of the betanaphtholdisulphonic acids was commenced by one of the authors in 1880 (*Chem. Soc. Journ.*, 1881, 139). Results were obtained which led to the belief that both were derivatives of the Schaefer monosulphonic acid, but at that time no methods were available by which any final determination of their constitution could be effected. Subsequently attention was directed to the corresponding amido-disulphonic acids when these became procurable. About

three years ago a liberal supply of the betanaphthylaminedisulphonic acid R, in the form of acid sodium salt, was obtained from the Actiengesellschaft für Anilinfabrikation, through the kindness of Dr. Martius. In the spring of 1888, the authors became aware of the results since published by Duisberg and Pfitzinger (*Ber.*, 1889, 396), and arranged with Dr. Duisberg to carry on the investigation.

Constitution of the betanaphthylaminedisulphonic acid R.—Duisberg and Pfitzinger inferred that this acid was derived from the α-naphthalenedisulphonic acid of Ebert and Merz, as the disulphonic acid obtained from it on displacing the NH_2-group by v. Baeyer's hydrazine process gave the dihydroxynaphthalene corresponding to the α-acid on fusion with potash. Although perfectly satisfied with this proof, the authors have thought it desirable to amplify the evidence in order to meet the possible objection that isomeric change may occur during the fusion, as in the case of benzene-derivatives. They find on directly comparing the disulphonic acid with the Ebert and Merz α-acid, that the two behave alike; the sulphochloride derived from the amido-acid crystallising from benzene in large prisms which gradually become opaque, fusing at 158°, and yielding the dichloronaphthalene melting at 114° on distillation with PCl_5.

By the Sandmeyer method the amido-acid may be converted into a chlorodisulphonic acid, the chloride of which crystallises in radiate groups of spear-like needles, melting at 165°; on distillation with PCl_5 this yields a corresponding trichloronaphthalene, which crystallises from alcohol in small spherical aggregates of minute scales or flat needles melting at 90—91°.

Taking into account the previous determination of the constitution of the Ebert and Merz α-acid (*cf.* these Proceedings, 1888, 48), the constitution of the amidodisulphonic acid R and of the corresponding trichloronaphthalene is expressed by the formulæ:—

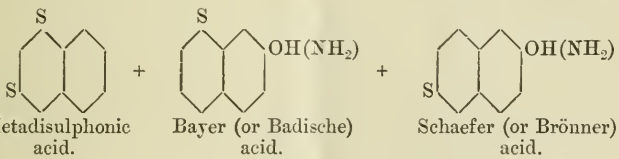


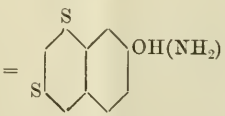
Betanaphthylamine-disulphonic acid R.

Trichloronaphthalene. M. p. 90—91°.

Constitution of betanaphthylaminedisulphonic acid G.—A quantity of this acid was first procured from the Actiengesellschaft für Anilinfabrikation; we have to thank the Farbenfabriken vormals F. Bayer and Co. for a subsequent larger supply. On converting it into naphthalenedisulphonic acid by the hydrazine method, a new acid was obtained. The *barium* salt, $C_{10}H_6(SO_3)_2Ba,4H_2O$, is very soluble in water, and has not been obtained in any definite crystalline form; it retains $1\frac{1}{2}H_2O$ at 270°, above which temperature it decomposes.

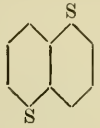
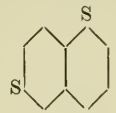
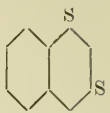
The *potassium* salt, $C_{10}H_6(SO_3K)_2,2H_2O$, is very soluble, but crystallises well in small prisms. The sodium salt is very soluble, and has not been obtained in a form fit for analysis. The chloride, $C_{10}H_6(SO_2Cl)_2$, crystallises from benzene in prisms, from acetic acid in prismatic needles, and from petroleum spirit in small needles; it melts at 137°, and on distillation with PCl_5 yields a dichloronaphthalene melting at 61·5°, convertible by sulphonation, &c., into a sulphochloride melting at 147°. The acid is therefore the meta-disulphonic acid of naphthalene. The relative position of the sulphonic radicles being thus determined, their position relatively to the β-NH_2 radicle may be inferred from the facts that the hydroxy-G-acid is obtained as direct sulphonation-product of the Bayer modification of betanaphtholsulphonic acid, and that it yields the isomeric Schaefer acid when reduced by sodium amalgam; the authors first became acquainted with the latter fact from Dr. Caro, and have verified it in the course of an experimental examination of the behaviour of substituted naphthalenesulphonic acids generally on reduction: the details of this work will be given later on, but it may be here stated that, although the sulphonic acids are usually reducible to naphthalene in the manner first pointed out by Otto in the case of naphthalene-α-sulphonic acid, the β-sulphonic derivatives are far less readily affected; the NH_2 radicle also exercises a special protecting influence in many cases. Superposing the various results, the constitution of the G-acids is shown to be as follows:—

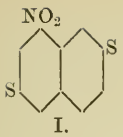




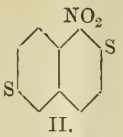
Hydroxy(amido)-disulphonic acid G.

The G-acid is convertible by Sandmeyer's method into a chlorodisulphonic acid the chloride of which crystallises from benzene in long radiate needles, melting at 170°; this is converted by PCl_5 into a trichloronaphthalene which crystallises in very slender needles melting at 113°, identical with that obtained by Alén (*Ber. Referate*, 1884, 437) from an α-nitro-acid prepared by nitrating the chloride of the β-disulphonic acid of Ebert and Merz. This result confirms the conclusion above arrived at, as of the three possible formulæ of Alén's acid:—

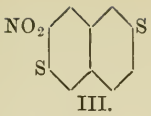
	1 : 4′	2 : 2′	2 : 3′	1 : 3′	1 : 3
S = SO_3H.					
$(SO_3H)_2$	Armstrong (*Chem. Soc. Journ.*, 1871, 173; *Ber.*, 1882, 205); Armstrong and Wynne (*C.S. Proc.*, 1886, 231; 1887, 42). Ewer and Pick, G. P. 41934	Ebert and Merz (*Ber.*, 1876, 592)	Ebert and Merz (*Ber.*, 1876, 592)	Armstrong and Wynne (*C. S Proc.*, 1886, 231); Armstrong (*C. S. Proc.*, 1889, 10). Ewer and Pick, G. P. 45229	Armstrong and Wynne.
$(SO_3)_2Ba$	+ $4H_2O$, granules consisting of microscopic needles	+ $2H_2O$, long, broad needles	+ H_2O, " crusts "	+ $4H_2O$, granules consisting of microscopic needles	+ $4H_2O$, no definite form. Granular, very soluble.
$(SO_3K)_2$	+ $2H_2O$, in prismatic needles..	+ $2H_2O$, in needles	Needles	+ H_2O, granules, consisting of microscopic needles	+ $2H_2O$, small prismatic forms. Very soluble.
$(SO_3Na)_2$	+ $2H_2O$, glistening scales	+ $6H_2O$, in lustrous needles	+ H_2O, crystalline aggregates	+ $7H_2O$, long, broad needles	Very soluble in water.
$(SO_2Cl)_2$.....	Needles which become opaque. M. p. = 183°	Prisms which become opaque. M. p. = 158°	Needles. M. p. = 216°	Aggregates of small needles. M. p. = 127°	Prisms or prismatic needles, M. p. = 137°
Cl_2.....	Needles. M. p. = 107°.....	Scales. M. p. = 114°	Flat needles. M. p. = 136°	Needles. M. p. = 48°...	Needles. M. p. = 61·5°.



I.



II.



III.

II and III are excluded by the fact that the trichloronaphthalene corresponding to III melts at 90—91° (*vide supra*), and that corresponding to II also at about the same temperature (*cf.* these Proceedings, 1889, 52).

The results now obtained show that, as in the case of the Bayer and Badische monosulphonic acids, the action of diazo-salts on the G-disulphonic acids is either retarded or prevented by the "protecting influence" exercised by an α-1′-sulphonic group.

The properties of the five known naphthalenedisulphonic acids are summarised in the appended table.

The authors wish it to be understood that they *entirely reserve* the investigation of the metadisulphonic acid *and of its derivatives;* this being the third acid of the series of which they have first investigated the preparation and properties, they believe they are justified in claiming this privilege.

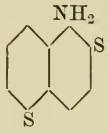
8. "Studies on the constitution of tri-derivatives of naphthalene. No. 2. α-Amido-1 : 3′-naphthalenedisulphonic acid." By Henry E. Armstrong and W. P. Wynne.

The 1 : 3′-naphthalene-$\alpha\beta$-disulphonic acid first described by the authors (these Proceedings, 1886, 231; 1889, 10) has acquired considerable interest and technical importance on account of the peculiar behaviour of the amido- and corresponding hydroxy-acid prepared from it and the dye-stuffs which the amido-acid affords (*cf.* Bernthsen, *Ber.*, 1889, 3327). This amido-acid has been patented by the Actiengesellschaft für Anilinfabrikation, in whose laboratory it was first prepared by M. Andresen (*cf.* Schultz, *Ber.*, 1890, 77) by nitrating our acid and reducing the nitro-derivative. We were naturally interested in determining the constitution of the amido-acid, and soon after it became known were favoured with a supply of material by the Actiengesellschaft für Anilinfabrikation. Technically, it has become known as α-naphthylamine-ϵ-disulphonic acid; but it appears very undesirable to perpetuate the confusion in nomenclature which reigns supreme in the case of the α-naphthylamine-acids by adopting and continuing this name.

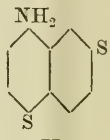
We first satisfied ourselves that the amido-acid had been prepared from our $\alpha\beta$-disulphonic acid by reducing it by the hydrazine method; the acid obtained gave a sulphochloride melting at 127°, and a dichloronapthalene melting at 48°.

The corresponding chlorodisulphonic acid was then prepared by Sandmeyer's method: the disulphochloride of this acid crystallises from petroleum spirit in tufts of very slender needles melting at 110°; on distillation with PCl_5, it is converted into a trichloronaphthalene which appears to be dimorphous, crystallising from alcohol either in long, slender needles melting at 87°, or in large, flat prisms melting at 90°.

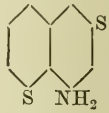
As the amido-acid is known to yield α-naphthylamine when deprived of its sulphonic groups, there are only three formulæ which can be assigned to it:—



I.



II.



III.

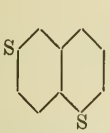
Formula I is precluded, as the corresponding trichloronapthalene melts at 78° (these Proceedings, 1889, 49); formula II is likewise precluded, as the corresponding trichloronaphthalene (*vide infra*) melts at 66° and 56°; formula III therefore expresses the constitution of the acid. This result confirms and is confirmed by the conclusions arrived at by Bernthsen, who finds that the corresponding hydroxy-acid exhibits the behaviour of the 1 : 1′-hydroxy-sulphonic acid, readily yielding a naphthalene - *sulphonelactone* - sulphonic acid. Although slightly longer than the name proposed by Bernthsen, this latter appears to us to be preferable. The present tendency to construct a name on rational principles, so as to express the nature of the substance designated, and then to deprive it of all meaning by elision of the significant syllable, is most irrational; the term *sulphonelactone* is expressive, and not inelegant; Erdmann's term, sultone, conveys no meaning to the uninstructed ear.

9. "Studies on the constitution of the tri-derivatives of naphthalene. No. 3. Alphanaphthylaminedisulphonic acid Dahl No. III. The constitution of naphthol-yellow S." By Henry E. Armstrong and W. P. Wynne.

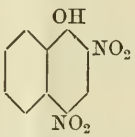
It is well-known that when alphanaphthol is sulphonated by excess of sulphuric acid, it is readily converted into acids capable of yielding naphthol-yellow S, a most valuable dye-stuff, the sulphonic acid of dinitroalphanaphthol, on treatment with nitric acid; although it is known that the yellow is a heteronucleal derivative and that the sulphonic group is in a β-position, inasmuch as it yields 1 : 2 : 4-sulphophthalic acid on oxidation (*cf.* Græbe and Rée, *Chem. Soc. Trans.*, 1886, 522), the position of this group has not hitherto been

determined. With the object of ascertaining the constitution of the yellow, the authors have examined the alphanaphthylaminedisulphonic acid No. III, prepared by sulphonating naphthionic acid with 35 per cent. anhydrosulphuric acid at a temperature not exceeding 30°, described in the German patent No. 41,957, 1886, of Dahl and Co., this acid being very readily converted into the yellow by diazotising and then heating with nitric acid. Through the kindness of Dr. Caro, a considerable quantity of this acid was obtained from the Badische Anilin und Sodafabrik.

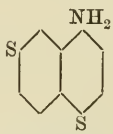
When reduced by the hydrazine method, the Dahl No. III acid is found to yield the authors' 1 : 3′-naphthalenedisulphonic acid; the sulphochloride actually prepared from the acid melted at 127°, and the corresponding dichloronaphthalene at 49°. Taking into account the fact that naphthol-yellow S is a heteronucleal β-sulphonic derivative, this result is alone sufficient to determine the constitution of the yellow and of the amido-acid, thus—



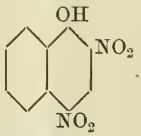
1 : 3′ naphthalene-disulphonic acid.



Dinitro-alpha-naphthol.



Dahl acid No. III.



Naphthol-yellow S.

The chlorodisulphonic acid prepared from the Dahl acid yields a sulphochloride very soluble in benzene, from which it crystallises in small prisms; it separates from petroleum spirit in rosettes of small, apparently rectangular prisms melting at 107°. The corresponding trichloronaphthalene affords a remarkable case of dimorphism: it is sparingly soluble in hot alcohol, from which it crystallises in slender needles melting at 66°; if the melting point be redetermined as soon as solidification has taken place, it is found to be 56°, but if determined after a longer interval 66°, as in the first instance. This trichloronaphthalene should be identical with that prepared by Widman from dichloronaphthalene-β-sulphonic chloride, which the authors have shown to be a derivative of 1 : 4-dichloronaphthalene (*cf.* these Proceedings, 1888, 106), but Widman's product is said to melt at 56°; the authors find, however, on preparing it according to Widman's direction, that it also melts at 66° or 56°. By nitrating

1 : 3′-η-dichloronaphthalene Cleve obtained a nitrodichloronaphthalene yielding a trichloronaphalene melting at 65°; the author's observations show that this is in reality identical with the Widman trichloronaphthalene, and therefore that the behaviour of 1 : 3′-dichloronaphthalene on nitration is perfectly "normal," and strictly comparable with that of both α- and β-monochloronaphthalene.

By sulphonating 1 : 4-chloronaphthalenesulphonic acid in the form of potassium salt by means of the theoretical proportion of sulphuric anhydride employed as 20 per cent. anhydrosulphuric acid at 100°, the authors have obtained a chlorodisulphonic acid identical with that prepared from the Dahl amido-acid : showing that the α-chloro-, α-amido- and α-hydroxy-monosulphonic compounds behave similarly on further sulphonation; but it remains to be ascertained whether the series of changes leading up to the production of the final stable compounds is identical in the several cases.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Travaux de la Station Agronomique de l'École d'Agriculture de Grignon, par P. P. Deherain. Paris 1889. From the Author.

Death in the Pot; a Treatise on Adulterations of Food and Culinary Poisons, and Methods of Detecting them, by F. Accum. London. From Hy. Bassett, Esq.

II. *By Purchase.*

Chemie der menschlichen Nahrungs- und Genuss-mittel, von J. König. 3te Aufl. Band I. Berlin 1889.

Traité de Chimie générale, par P. Schützenberger. Tome VI. Paris 1890.

Handbuch der chemischen Technologie, von R. v. Wagner. 13te Aufl. neu bearbeibet von F. Fischer. Leipzig 1889.

Lehrbuch der gerichtlichen Chemie, von G. Baumert Erste Abtheilung. Braunschweig 1889.

At the next meeting, on February 20th, the following papers will be read:—

The behaviour of the more stable oxides at high temperatures. By G. H. Bailey, D.Sc., and W. B. Hopkins.

The influence of different oxides on the decomposition of potassium chlorate. By G. J. Fowler, M.Sc., and J. Grant.

Note on ammonium hypochlorite. By C. F. Cross and E. J. Bevan

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Issued 27/2/1890.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 78. Session 1889–90.

February 20th, 1890. Dr. W. J. Russell, F.R.S., President, in the Chair.

Messrs. Frank H. Mason, A. H. McConnell, Edward Russell, John Wade and S. Russell Wells, were formally admitted Fellows of the Society.

It was announced that the following changes in the Council list were proposed by the Council :—

As *Vice-Presidents:* Professors Crum Brown, F.R.S., and W. N. Hartley, F.R.S.; *vice* Prof. McLeod, F.R.S., and Mr. Ludwig Mond.

As *Members of Council:* Messrs. Henry Bassett, C. F. Cross, Professor R. Meldola, F.R.S., and Mr. M. M. P. Muir; *vice* Professors A. H. Church, F.R.S., and F. Clowes, Mr. C. W. Heaton, and Dr. H. F. Morley.

Messrs. Bernard Dyer, R. H. Davies and R. J. Friswell were appointed by the meeting to audit the Treasurer's accounts.

Certificates were read for the first time in favour of Messrs. William Frede. ck Laycock, Ph.D., 2, Park Street, Dewsbury; Arthur Sheridan Lea, Caius College, Cambridge; George Müller, 125, Mercer Street, Jersey City, N. Jersey, U.S.A.; E. H. Neville, M.A., Sidney College, Cambridge; Ernest George Scott, Mayer Hall, near Birkenhead; Willie Brewin Shuttlewood, Hong Kong; Frederick Richard M. Stone, 64, Thomas Street, Merthyr.

The following papers were read :—

10. "The behaviour of the more stable oxides at high temperatures." By G. H. Bailey, D.Sc., Ph.D., and W. B. Hopkins.

The authors chiefly devote attention in this notice to oxide of copper. Previous experimenters had obtained cuprous oxide by

heating the oxide to redness. From the results obtained by the authors, it appears that at higher temperatures oxygen is given off, and that an oxide having the composition Cu_3O is formed. This is insoluble in mineral acids and even in boiling aqua regia; it can, however, be changed into a soluble form by fusion with caustic potash, from which it separates on treatment with water. The oxides of lead and tin seem to behave like that of copper at high temperatures.

11. "The influence of different oxides on the decomposition of potassium chlorate." By G. J. Fowler, M.Sc., and J. Grant.

The object of the experiments has been to systematically examine the influence of the chief metallic oxides and certain unstable salts on the decomposition of potassium chlorate. Upwards of a hundred experiments have been made, the most significant of which are recorded in the paper. In each case, the temperature at which oxygen is evolved, the amount of chlorine given off and the composition of the residue after heating have been determined. The variation of the results according to the acid or basic character of the oxide added, its physical condition and the relative masses of the oxide and chlorate has been recorded.

The results obtained may be summarised as follows :—

(1.) Acid oxides, such as V_2O_5, WO_3 and U_3O_8, cause the evolution of oxygen at a reduced temperature; a metavanadate, tungstate or uranate being formed. Chlorine is evolved in these cases in large quantity, but the whole of the oxygen of the chlorate is not evolved, as the compound of K_2O with the oxide is not decomposed either by heat or by chlorine: $4KClO_3 + 2V_2O_5 = 2K_2OV_2O_5 + 2Cl_2 + 5O_2$.

(2.) Alumina probably acts similarly but less energetically, the attraction between the K_2O and Al_2O_3 not being so great.

(3.) In the case of chromium sesquioxide, the oxygen is evolved at a reduced temperature, accompanied by chlorine. The decomposition may be supposed to be brought about by the affinity of the Cr_2O_3 for O and the affinity of the CrO_3 thus formed for K_2O, but all the oxygen of the chlorate is not evolved, since $8KClO_3 + 2Cr_2O_3 = 4K_2CrO_4 + 4Cl_2 + 7O_2$.

(4.) In the case of the sesquioxides of iron, cobalt and nickel, cupric oxide and manganese dioxide, oxygen is evolved at a comparatively low temperature accompanied by only a little chlorine; the oxide is left but little altered at the end of the experiment.

Accepting McLeod's theory of the action of manganese dioxide (*Chem. Soc. Trans.*, 1889, 184), which is fully in harmony with the results of the experiments under consideration, it would seem that

manganese dioxide first acts by reason of its affinity for oxygen and the affinity of the higher oxide thus formed for K_2O. The permanganate first formed, however, is unstable (here there is a difference between the oxides of this class and those of the preceding), and is resolved into $K_2MnO_4 + MnO_2 + O_2$. The K_2MnO_4 is decomposed by chlorine into KCl and MnO_2, which is thus regenerated. The addition of sodium carbonate retards the evolution of oxygen, probably because the manganate is thereby rendered more stable. The action of the other oxides (*cf.* Spring and Prost) of this class can, it is believed, be explained in a similar manner to that of manganese dioxide.

(5.) The monoxides of barium, calcium and lead cause no evolution of oxygen when heated with chlorate, but the latter breaks up below its normal temperature of decomposition, potassium chloride and a peroxide being formed. Here the affinity of the oxide for oxygen induces change.

(6.) On the other hand, potassium chlorate may act as a reducing agent in the presence of such oxides as silver oxide and the peroxides of barium and lead, a perchlorate being formed. No oxygen is evolved. Here the change is brought about by the affinity of the chlorate for oxygen. In the case of the oxides of calcium, barium and lead, the extent to which the chlorate is oxidised evidently depends on the relative masses of the interacting substances.

(7.) Water of hydration appears to diminish the activity of an oxide, owing doubtless to the absorption of heat necessary for its conversion into steam.

(8.) The physical condition of the oxide is of influence. Copper oxide prepared in the dry way is almost inactive.

(9.) Certain substances, although apparently they undergo no chemical change, assist the decomposition, *e.g.*, powdered glass, sand and kaolin.

(10.) Oxides such as those of zinc and magnesium are inactive.

Discussion.

Dr. Hodgkinson said that he had noticed that all the chlorine was expelled from potassium chlorate by heating it with either uranic or tungstic or vanadic oxide—was this because these oxides expel the chlorine from chlorides? In the case of stannic oxide, everything depended on the state of the oxide: the native form had no action, but metastannic acid expelled chlorine.

Professor McLeod thought that the decomposition of potassium chlorate was promoted in some cases by a mere action of presence similar to that which charcoal exercises on the boiling of water: for

instance, platinum black appeared to act in this way, and probably basic oxides exercised a similar influence.

Professor RAMSAY expressed the opinion that in some cases the oxides were converted into corresponding chlorates: that copper oxide, for instance, became converted into copper chlorate, which was thereupon resolved into copper oxide and an unstable oxide of chlorine; it was desirable from this point of view to study the behaviour of various chlorates.

Professor THORPE said that much had already been done in the direction suggested by Professor Ramsay; but difficulty arose as many chlorates were hydrated salts which decomposed during dehydration. After calling attention to Teed's and Frankland and Dingwall's experiments, he said there was no evidence that when, for example, manganese dioxide was used manganese chlorate was formed. Mr. Eccles had several years ago made experiments in his laboratory to test this point, and had found that no alkali was formed when manganese dioxide was used, as must have been the case if any chlorate of the oxide were produced. The non-production of perchlorate was the most remarkable feature of the change in presence of manganese dioxide (*cf. Chem. Soc. Journ.*, 1876, 856).

In reply to a remark by Professor Ramsay, Professor MCLEOD said that the formation of permanganate accounted for the fact that no alkali was obtained, although chlorine was given off.

12. "The interaction of hypochlorites and ammonium salts. Ammonium hypochlorite." By C. F. Cross and E. J. Bevan.

No mention is made of ammonium hypochlorite in the later textbooks and dictionaries; in the last edition of *Gmelin* (vol. 2, 479), however, there is a short paragraph headed "Ammonium hypochlorite?" in which its probable existence is spoken of on the authority of Schönbein. This chemist observed that a pungent odour is developed when ammonia is added to chlorine-water, and that the liquid exhibits bleaching powers and the property of decomposing hydrogen peroxide with liberation of oxygen: hence it was supposed that the destructive action of chlorine on ammonia is preceded by the formation of ammonium hypochlorite.

The authors have recently had occasion to study the subject more closely. On treating a dilute solution of bleaching powder with the equivalent quantity of an ammonium salt, no sensible loss of "available chlorine" takes place provided interaction occur at a low temperature (10°). The pungent odour already mentioned as noticed by Schönbein suggested that the resulting compound was volatile, and, therefore, in order to obtain evidence as to its composition, a current of air was passed through the solution and subsequently

through water and through a solution of potassium iodide acidified with normal acid; eventually the liberated iodine was titrated with thiosulphate and the excess of acid was determined in the same solution by means of normal alkali. The iodine liberated was taken as equivalent to the chlorine, and the amount of acid saturated as equivalent to ammonia; the results obtained were—

(1.) Cl = 0·0365	NH_4 = 0·0090	2·06 : 1
(2.) Cl = 0·0316	NH_4 = 0·0081	1·98 : 1.

These correspond with the formula NH_4OCl, in which the ratio of oxidising chlorine to ammonium is that of 2Cl : NH_4. Further evidence as to the composition of the compound was obtained by extracting the aqueous solution with ether, and after diluting the extract with alcohol adding potassium iodide and the necessary quantity of thiosulphate: the resulting mixture was neutral. The compound was also volatilised by means of a current of air, which was then washed and passed into a solution of sodium sulphite; the oxidation of the sulphite was the only change observed, the solution remaining neutral, whereas had no ammonia been present it would necessarily have been acid.

The evidence of the formation and existence of ammonium hypochlorite in solution would seem, therefore, to be complete; the isolation of such a compound, however, would necessarily be attended with considerable difficulty, and all attempts in this direction have hitherto failed to give a result.

At ordinary temperatures solutions prepared as described containing from 1 to 2 grams Cl per 100 lose oxidising chlorine comparatively rapidly: thus one containing 1·6 grams per 100 immediately after preparation contained after filtering and standing 2 hours 0·12 gram; after 48 hours 0·06, and after 72 hours 0·04.

The ammonia product presents curious anomalies in oxidising properties in comparison with other hypochlorites: thus it is without action on many colouring matters, *e.g.*, those of the vegetable fibre; a solution tinged with a drop of a solution of indigo sulphonate retains its colour for some hours, although it at once liberates iodine from potassium iodide; and it does not peroxidise hydrated lead oxide, nor does it oxidise potassium ferrocyanide in presence of acetic acid. But it oxidises sulphites and arsenites, and its effect on aniline salts is identical with that of ordinary hypochlorites.

The compound is easily formed by the electrolysis of ammonium chloride solutions.

Discussion.

Professor Ramsay said that a few months ago he also had attempted to prepare ammonium hypochlorite, and had found that on

adding ammonia to hypochlorous acid nitrogen was not given off. It was to be noted that the formula of ammonium hypochlorite was equivalent to that of hydroxylamine hydrochloride.

In answer to Professor Dunstan, Mr. Cross said that the addition of acid did not alter the properties of the liquid as an oxidising agent.

Dr. Armstrong suggested that probably the authors were dealing with a chlorinated derivative of ammonia, *e.g.*, NH_2Cl: Gattermann's experiments show that such compounds are more stable than is usually supposed.

13. "The action of phosphoric anhydride on stearic acid." By F. Stanley Kipping, Ph.D., D.Sc., Heriot Watt College.

It is stated in both editions of *Beilstein* that when stearic acid is heated with phosphoric anhydride it yields a compound of the formula $C_{18}H_{34}O$, melting at 54—56°, insoluble in potash. As the formation of a compound so related to the acid in this manner appeared remarkable, being I believe, without a parallel, I have re-examined the subject, and am led to give a brief account of my results in order to reserve the study of this and similar changes.

If stearic acid be heated at about 200° in an oil-bath, and about an equal weight of phosphoric anhydride be added in small portions at a time, the whole being well stirred, a considerable quantity of gas is evolved and a black, tarry mass is obtained. The mixture is allowed to cool, then stirred with water and the whole boiled for some time with a large excess of moderately concentrated potash in order to remove the phosphoric acid. A dark-brown, almost black oil collects on the surface and, on cooling, solidifies to a soft, waxy cake; this product is separated from the alkaline solution, washed with water, transferred to a flask and repeatedly extracted with boiling dilute alcohol. The alcoholic extracts deposit, on cooling, a yellowish, flocculent substance, and there remains in the flask a dark-brown, waxy mass which is very sparingly soluble in dilute alcohol; this residue is being investigated.

The compound which separates from the alcoholic solution can be obtained in a colourless condition by repeatedly recrystallising it from alcohol and ether. It crystallises in colourless, waxy, microscopic plates, and is only sparingly soluble in cold ether and alcohol, but much more readily in the warm solvents and in benzene; it seems to be insoluble in hot potash or in ammonia. When heated slowly in a capillary tube it begins to soften at 73° and melts completely at 75—76°, or about 3° higher than stearic acid. On combustion, 0·1420 gram gave 0·4316 gram CO_2 and 0·1771 gram H_2O.

	$C_{18}H_{34}O$.	$C_{18}H_{36}O_2$.	$C_{35}H_{70}O$.	Found.
C =	81·20	76·27	83·00	82·88 per cent.
H =	12·78	12·68	13·83	13·85 ,,
O =	6·02	11·05	3·17	3·27 ,,

The results show clearly that the compound is not simply unchanged stearic acid, a fact which is further proved by the higher melting point, and that it has not the composition $C_{18}H_{34}O$ is apparent from the high percentage of hydrogen which it contains. The results of the analysis agree very closely with the formula $C_{35}H_{70}O$, and the experiment described below confirms this conclusion.

It seems, then, that when stearic acid is heated with phosphoric anhydride, under the conditions described above, one of the products is stearone, and that action takes place according to the equation: $2C_{17}H_{35}\cdot COOH = (C_{17}H_{35})_2CO + CO_2 + H_2O$. Quantitative experiments have not yet been made, but the yield appears to be as good, or better, than that obtained in preparing stearone by the distillation of salts of stearic acid.

Stearone has been previously prepared by Heintz (*Jahresb.*, 1855, 515, 516) by distilling stearic acid alone or with lime ; Heintz gives 87·8° as the melting point, whereas the compound obtained as described above melts at 75—76°. The cause of this difference has not yet been ascertained, but it is probably due to the presence of impurities too small in quantity to have any effect on the analysis. The stearic acid employed melted at about 62° ; the experiments will be repeated with the pure acid.

Stearonehydroxime $(C_{17}H_{35})_2C{:}N\cdot ON$. A small quantity of the colourless, crystalline compound (m.p. 75—76°) was dissolved in warm alcohol and boiled for about three hours with excess of hydroxylamine and a large excess of potash. On cooling the solution and adding water, a colourless, flocculent substance was precipitated; the solution was filtered, the precipitate washed repeatedly, first with dilute hydrochloric acid and then with water, and dried on a porous plate. 0·2514 gram gave 6·6 c.c. of nitrogen at 755 mm. and 40°, or 2·67 per cent.; the theoretical percentage corresponding to the formula $C_{35}H_{71}NO$ is 3·07 per cent. This hydroxime is a colourless, seemingly amorphous compound readily soluble in benzene and warm alcohol, but insoluble in acids and in alkalis. When heated very slowly in a capillary tube, it begins to soften at about 53° and melts completely at 58—59°. It separates from alcohol as a powder which, when examined under the microscope, appears to be perfectly homogeneous.

14. "Semithiocarbazides." By Augustus E. Dixon, M.D.

Orthotolylphenylsemithiocarbazide (from *o*-tolylthiocarbamide and

phenylhydrazine) forms vitreous prisms melting at 162—163°. It is nearly insoluble in water; soluble in alcohol, ether and chloroform.

Phenylorthotolylsemithiocarbazide (from phenylthiocarbimide and *o*-tolylhydrazine) is isomeric with the preceding. It forms long, pearly-white prisms melting at 145—146°; it is nearly insoluble in water, but dissolves freely in alcohol, ether and chloroform.

Methylphenylsemithiocarbazide forms delicate, silky needles melting between 88° and 89°. It is somewhat soluble in hot water; very soluble in alcohol and in chloroform.

Ethylorthotolylsemithiocarbazide crystallises from alcohol, in which it is rather freely soluble, in fine, white needles possessing a faint pink tinge. It melts at 129—130°; is insoluble in cold water, but dissolves freely in ether and chloroform.

Allylphenylsemithiocarbazide separates from benzene in tangled masses of silvery-white, flexible needles, which become highly electrical on friction; it melts at 118—119° to a bluish-green liquid. It is soluble in ordinary solvents, but is precipitated from solution in benzene by light petroleum.

These compounds all give with concentrated sulphuric acid solutions varying in colour from greenish-blue to deep azure. They are desulphurised, either with great difficulty, or not at all, by boiling alkaline lead tartrate; but readily yield their sulphur to ammoniacal silver nitrate. With $CuSO_4$ or Fe_2Cl_6 they afford strongly-marked colour changes.

The connexion between the solubility and fusibility of the several compounds is traced, and it is shown that, as a rule, Carnelley's principle holds good that the greater the solubility the lower is the melting point; the author also suggests an application of Carnelley's principle to connect the melting points with the molecular structure.

15. "Note on the production of ozone by flames." By J. Tudor Cundall, B.Sc., University College, Cardiff.

It is stated by L. Ilosvay de N. Ilosva (*Ber. Referate*, 1889, 791 *et seq.*) that when the products of combustion of various kinds of flames are collected, they do not exhibit the smell and taste of ozone. This is confirmed by the results of some unpublished experiments made by the author in a similar manner in 1886.

Recently, however, the author has found that the air aspirated through a tube (3 mm. in bore) whose mouth is fixed about 5 mm. above the tube, and 5 mm. away from the flame, of a Bunsen burner, both tastes and smells strongly of ozone. Similar results were obtained both from luminous and hydrogen flames.

It was not found possible to confirm this fact by any other test for

ozone, owing to the impossibility of finding any which was sufficiently sensitive which was not common to it and dilute nitrogen oxides. At first sight, it seemed that Houzeau's papers (impregnated with red litmus and potassium iodide) would give the necessary distinction, as an acid gas could not be expected to give an alkaline product. Ilosva states, however, that nitrogen oxides turn these papers blue, and the author has confirmed this result.

Papers impregnated with thallium hydroxide were employed with negative results, but, on testing them in a stream of ozonised oxygen from a Siemens tube, they were found to be far from sensitive. The same applies to an acidified solution of sulphanilic acid and α-napthylamine, which certainly gives a yellow colour with a fair amount of ozone, but this colour is completely masked by the rose-red produced by small traces of nitrogen oxides which may be present simultaneously.

The gas aspirated in this way both from coal gas and hydrogen flames gave definite indications with mercury of the peculiar behaviour of ozone, but the quantity present was not sufficient to make the mercury adhere completely to its containing flask.

In conclusion, the author agrees with Ilosva in so far that he regards the smell and taste of ozone as the only tests for it that are at all reliable when it is present only in traces, but differs from him as regards its formation in flames; although nitrogen oxides are undoubtedly formed in flames, yet at the same time ozone can be detected by aspirating the air surrounding the flame in such a manner as to get a minimum of the products of combustion and at as low a temperature as possible.

ANNIVERSARY MEETING.

The anniversary meeting will be held at *Four o'clock in the Afternoon* of Thursday, March 27th next.

It is arranged that, in the evening of the same day, the Fellows and their friends will dine together at the Whitehall Rooms, Hôtel Métropole (entrance in Whitehall Place). Dinner will be on the table at seven for half-past seven o'clock. Fellows intending to be present are particularly requested to give notice by means of a post-card which they will receive for the purpose not later than Saturday, March 22nd. Price of dinner, including wine, One Guinea.

It is proposed to hold a special meeting of the Society on Thursday, May 8th, for the exhibition of new interesting apparatus or specimens. Fellows who desire to exhibit objects are requested to communicate with the Secretaries.

At the meeting on March 20th, Professor Judd, F.R.S., will deliver a lecture on *the evidence afforded by petrographical research of the occurrence of chemical change under great pressures.*

At the next meeting, on Thursday, March 6th, the following candidates will be balloted for:—

1. Anderson, Frederick Alfred, B.Sc., Lesney House, Erith, Kent.
2. Babington, Percival, Elmfield, Rotherham, Yorks.
3. Beardmore, G. Russell, M.D., Warwick House, Upper Street, Islington.
4. Berncastel, Richard, 38, Ventnor Villas, Brighton.
5. Blount, Bertram, 1, Broadway, Westminster.
6. Blake, Robert Frederick, 37, Hartington Street, Dublin Road, Belfast.
7. Bunting, Henry Herbert, 82, Netherwood Road, Kensington, W.
8. Burton, William, 18, Victoria Street, Stoke-on-Trent.
9. Cobbold, Paul Alexander, Warwick School, Warwick.
10. Dennant, John, Lyndhurst Crescent, Glenferrie, Melbourne.
11. Gossling, Frank, Waldegrave Road, Teddington.
12. Jackson, John Charles, 51, Wellington Road, St. John's Wood.
13. Lumsden, John S., 5, Paradise Road, Dundee.
14. Macintyre, Alfred E., Saint John, N.B., Canada.
15. Mills, Frederick, Bevan Crescent, Stockton-on-Tees.
16. Moore, Ira, Sutton, Crosshills, *viâ* Keighley.
17. Myles, John, Butterburn Park, Hamilton.
18. Rothwell, Robert Richard, 82, Mawson Street, Ardwick Green, Manchester.
19. Sargeant, Edward, 75, Park Road, Bolton.
20. Valentin, Basil William, Acton Brewery, Birmingham.

The following papers will be read:—

"Crystalline products derived from various species of *Citrus*." By Professor Tilden, F.R.S., and C. R. Beck.

"Reduction of α-Diketones." By Dr. Japp, F.R.S., and Dr. Klingemann.

"Studies on Isomeric change. Halogen-derivatives of quinone." By A. R. Ling.

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Issued 12/3/1890

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 79. Session 1889–90.

March 6th, 1890. Dr. W. J. Russell, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. Joseph Barker, 8, St. James's Street, S.W.; Charles Ridgeway Beck, 181, High Street, Burton-on-Trent; David Corrie, Nobel's Explosives Company, Polmont Station, N.B.; Andrew Cowan Holborn, B.Sc., 10, West Garden Street, Glasgow; Herman Lescher, 61, Egerton Gardens, South Kensington; Henry de Mosenthal, 220, Winchester House, Old Broad Street, E.C.; James S. H. Walker, 304, Morningside Road, Edinburgh.

The following were elected Fellows of the Society:—Frederic Alfred Anderson, B.Sc., Percival Babington, G. Russell Beardmore, M.D., Richard Berncastel, Bertram Blount, Robert Frederick Blake, Henry Herbert Bunting, William Burton, Paul Alexander Cobbold, John Dennant, Frank Gossling, John Charles Jackson, John S. Lumsden, Alfred E. Macintyre, Frederick Mills, Ira Moore, John Myles, Robert Richard Rothwell, Edward Sergeant, M.D., Basil William Valentin.

The President announced that the senior Secretary would attend the meeting to be held in Berlin on March the 11th, to celebrate the 25th anniversary of Professor Kekulé's benzene theory, and would present the following address from the Society:—

"The President and Council of the Chemical Society, on behalf of British Chemists, desire to offer to Professor August Kekulé their warmest congratulations on the occasion of the Twenty-fifth Anniversary of the promulgation of his theory of the Constitution of Aromatic Compounds.

"The influence which the felicitous conception of Benzene as a closed chain has had on the development of chemical theory, the impetus which it has imparted to the study of the intricate problems of isomerism among the derivatives of this and similar compounds, and the guidance which it has afforded in an industry of such magnitude and importance as that of the Coal Tar Colours, is universally recognised; and it is with special pleasure that the countrymen of Faraday, the discoverer of Benzene, recount these benefits while paying honour to their author.

"This theory found the chemistry of even the immediate derivatives of benzene an almost untilled field; it has transformed it into a fertile province, to which have been annexed regions the very existence of which was unknown.

"May it long be permitted to you, Professor Kekulé, whose work has been so full of suggestion and inspiration, to remain witness to the benefits which continue to flow from your fruitful generalisation."

The following papers were read:—

16. "Some crystalline substances obtained from the fruits of various species of *Citrus*." By William A. Tilden, D.Sc., F.R.S., and Charles R. Beck.

The authors have examined the solid matters which are deposited from freshly extracted oils of limes, lemons, and bergamot made by hand. The substance from oil of limes (*C. limetta*), after purification by repeated crystallisations from alcohol containing a little potash, forms small, pale-yellow needles, united in tufts, which melt at 121—122°. It is proposed to name this substance *limettin*. It is neither an acid nor a glucoside. It is not acted on by acetyl chloride or by phenylhydrazine. Analysis leads to the formula $C_{16}H_{14}O_6$. When submitted to the action of bromine it affords a tribromo-derivative, $C_{16}H_{11}Br_3O_6$, which crystallises in colourless scales. When boiled with a concentrated solution of soda limettin loses an acetyl-group, yielding a substance very similar to itself in appearance and properties, $C_{14}H_{11}(OH)O_4$. When fused with potash it yields phloroglucol and acetic and formic acids.

Essence of lemon yields a substance similar to limettin in appearance, though the crystals are more lustrous and melt at 116°. Concordant analyses lead to the formula $C_{14}H_{14}O_6$, which contains 2C less than the formula of limettin.

Bergamot yields a crystalline compound differing from both the preceding. It forms colourless, distinct prisms melting at 270—271°.

The examination of this substance will be continued when a supply of material has been obtained.

These substances are entirely distinct from the compounds which, under the names of aurantiin, hesperidin, limonin, have been obtained by other chemists from various fruits of the orange and lemon tribe.

The two former of these are glucosides. Hesperidin has been shown to be a derivative of phloroglucol, and in its origin is probably connected with the substance described under the name limettin in this paper.

17. "Reduction of α-diketones." By Francis R. Japp, F.R.S., and Felix Klingemann, Ph.D.

Benzil was boiled for a few minutes with fuming iodhydric acid, and after removal of the iodine the product was distilled under reduced pressure: an excellent yield of *deoxybenzoïn* was obtained.

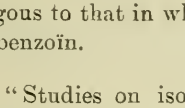
Phenanthraquinone, subjected to the same treatment, yielded the so-called *phenanthrone*, which Lachowicz, who prepared this compound by the reduction of dichlorphenanthrone (from phenanthraquinone and phosphorus pentachloride), regarded as the deoxybenzoïn of phenanthraquinone, $\begin{matrix} C_6H_4\cdot CO \\ | \quad\quad | \\ C_6H_4\cdot CH_2 \end{matrix}$; the authors, however, conclude that it is a phenol, viz., $\begin{matrix} C_6H_4\cdot C(OH) \\ \| \quad\quad | \\ C_6H_4\cdot CH \end{matrix}$, as it is not acted on by phenylhydrazine, and when heated with acetic anhydride forms an acetyl-derivative (m. p. 76—77°). When Lustgarten's test for β-naphthol (shaking the solution in caustic potash with chloroform) is applied to it, like β-napthol, it affords a strong Prussian blue coloration, the colouring matter separating in blue needles with a coppery lustre. This interaction is to be further studied.

By boiling phenanthraquinone with acetic acid, to which a small quantity of strong iodhydric acid together with some amorphous phosphorus had been added, *monacetylphenanthraquinol*,

$$C_{14}H_8(OH)(OC_2H_3O),$$

was obtained, identical with the compound prepared by Klinger (*Annalen*, **249**, 138) by the direct interaction of aldehyde and phenanthraquinone in sunlight.

By distilling acetylphenanthraquinol under reduced pressure, two compounds were obtained: a substance which distilled over, and which crystallised from benzene in red plates, melting at 155°, giving on analysis, C, 84·0, H, 4·7 per cent.; and a second substance, which sublimed into the neck of the flask, condensing in the form of needles, melting at 295—297°, and giving figures agreeing with the formula

$C_{28}H_{16}O$. The authors obtained a compound which they believe to be identical with this by heating acetylphenanthraquinol with concentrated chlorhydric acid at 200—210°; it is possibly *tetraphenylene-furfuran*,  ; the last-mentioned mode of formation being analogous to that in which lepiden (tetraphenylfurfuran) is obtained from benzoïn.

18. "Studies on isomeric change, No. IV. Halogen-derivatives of quinone (first notice)." By Arthur R. Ling.

The experiments of Hantzsch and of Nietzki have proved, in opposition to those of Levy, that the "anilic" acids are paradihydroxy-derivatives, and Hantzsch and Schniter have shown that an isomeric change occurs when paradichloroquinone is brominated, the product being metadichlorometadibromoquinone. The author has made several attempts to prepare paradichlorodibromoquinone, but hitherto unsuccessfully; in so doing he has obtained results which confirm Hantzsch and Schniter's conclusion.

Metadichlorodibromoquinone is formed on brominating paradichloroquinone or diacetylparadichloroquinol in acetic acid solution, also by the chlorination of paradibromoquinone, the isomeric change apparently occurring in the first and last mentioned cases at the ordinary temperature. By brominating diacetylparadichloroquinol dissolved in carbon tetrachloride in the presence of a trace of iodine, a diacetyldichlorobromoquinol has been obtained, which melts at 260—270°; this may, however, be a mixture of isomerides.

Metadichlorobromoquinone is obtained by brominating metadichloroquinone, and also together with the paradichloro-derivative by brominating paradichloroquinone. It forms yellow plates which do not show a sharp melting point (175—180°); it is sparingly soluble in cold alcohol, easily in boiling. On treatment with potash it yields chlorbromanilic acid. The quinol formed by reducing it with sulphurous acid separates from chloroform in white needles, melting at 135°, sparingly soluble in cold water or in chloroform but easily in the boiling liquids. On acetylation it yields a diacetyl-derivative which crystallises from alcohol in white needles melting at 174—180°.

Paradichlorobromoquinone is formed together with its isomeride on brominating paradichloroquinone. It is somewhat more soluble in the ordinary solvents than its isomeride, and melts at 158—159°. On treatment with potash it yields chloranilic acid.

Paradichlorobromoquinol crystallises from water in long, transparent, monohydrated needles which melt at 124—126°; they easily

lose their water, becoming opaque, and then melt at 132—135° Recrystallised from chloroform, the substance melts at 135·5°: it possesses about the same solubility in all the solvents tried as its isomeride. Hence the two cannot be separated by crystallisation. On acetylation it yields an acetyl-derivative, which crystallises in silky needles melting at 158—159°, sparingly soluble in cold dilute alcohol, but easily in boiling.

When paradichlorobromoquinone is brominated at the ordinary temperature, a product is obtained which may perhaps contain paradichlorodibromoquinone, since on treatment with potash it affords a mixture of chlorobromanilic and bromanilic acids. In this way the author hopes to succeed in isolating paradichlorodibromoquinone.

19. "Note on a phenylic salt of phenylthiocarbamic acid." By Augustus E. Dixon, M.D.

When heated together in equimolecular proportions at 140—150°, phenol and phenylthiocarbamide interact forming *phenylic* phenylthiocarbamide, NHPh·CSOPh, but the yield is very small; this salt forms octahedral crystals resembling sulphur in appearance, melting at 150°.

20. "Contributions to the chemistry of thiocarbamides. Interaction of benzyl chloride and of allyl bromide with thiocarbamide, phenyl- and diphenylthiocarbamides." By Emil A. Werner.

An account is given of the first part of an investigation of the action of benzyl chloride and allyl bromide on thiocarbamide and its different phenylated homologues. After reviewing the results already obtained by Claus, Bernthsen and Klinger, and Will and Rathke in the same direction, the following compounds are described:—

$C_8H_{10}N_2S$·HCl, m. p. 174°, and the base $C_8H_{10}N_2S$, m. p. 88°, from benzyl chloride and thiocarbamide.

$C_{14}H_{14}N_2S$·HCl, m. p. 112°, and the base $C_{14}H_{14}N_2S$, m. p. 81—82°, from benzyl chloride and phenylthiocarbamide.

$C_{20}H_{18}N_2S$·HCl, m. p. 152—153°, and the base $C_{20}H_{18}N_2S$, a viscid liquid, from benzyl chloride and diphenylthiocarbamide.

$C_4H_8N_2S$·HBr, m. p. 84°, from allyl bromide and thiocarbamide; the base could not be isolated in a pure state.

$C_{10}H_{12}N_2S$·HBr, a viscid liquid, from allyl bromide and phenyl thiocarbamide; the base forms a syrupy fluid which is very unstable.

$C_{16}H_{16}N_2S$·HBr, m. p. 170—171°, and the base $C_{16}H_{16}N_2S$, m. p. 57°, from allyl bromide and diphenyl thiocarbamide.

The decomposition of the bases by dilute sulphuric acid at 170° (Will's reaction) is studied, and it is shown that the primary thiocarbamide-derivatives behave in a different manner to the homologues.

Characteristic mercuro-chlorides possessing somewhat similar properties have been obtained from the several compounds: the compound $C_5H_{10}N_2S{\cdot}HCl{\cdot}HgCl_2$ may be taken as an example; it melts at 112°, and at 136° decomposes with loss of a molecular proportion of HCl and simultaneous alteration in the position of the alkyl-group (benzyl).

The sulphates and picrates of the bases are described, and in the case of the compound $C_4H_8N_2S{\cdot}HBr$, from C_3H_5Br and CSN_2H_4, a chromium alum has been obtained, $(C_4H_9N_2S)_2Cr_2(SO_4)_4{\cdot}24H_2O$.

Benzyl thiocarbamate ($CONH_2{\cdot}SC_7H_7$) and benzyl phenylthiocarbamate ($CONHC_6H_5{\cdot}SC_7H_7$) were incidentally prepared: both compounds combine with two molecular proportions of $AgNO_3$; the resulting products are immediately decomposed by ammonia in accordance with the equation: $NH_2{\cdot}CO{\cdot}S{\cdot}C_7H_7 + 2AgNO_3 + 2NH_3 = CO(NH_2)_2 + AgSC_7H_7 + AgNO_3 + NH_4NO_3$.

ANNIVERSARY MEETING.

The anniversary meeting will be held at *Four o'clock in the Afternoon* of Thursday, March 27th next.

It is arranged that, in the evening of the same day, the Fellows and their friends will dine together at the Whitehall Rooms, Hôtel Métropole (entrance in Whitehall Place). Dinner will be on the table at seven for half-past seven o'clock. Fellows intending to be present are particularly requested to give notice by means of the post-card which they have received for the purpose not later than Saturday, March 22nd. Price of dinner, including wine, One Guinea.

It is proposed to hold a special meeting of the Society on Thursday, May 8th, for the exhibition of new interesting apparatus or specimens. Fellows who desire to exhibit objects *are requested to communicate with the Secretaries.*

At the next meeting, on March 20th, Professor Judd, F.R.S., will deliver a lecture on *the evidence afforded by petrographical research of the occurrence of chemical change under great pressures.*

HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY, ST. MARTIN'S LANE.

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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 80. Session 1889-90.

March 20th, 1890. Dr. W. J. Russell, F.R.S., President, in the Chair.

Messrs. Bertram Blount, S. Home Collins, F. H. Perry Coste, T. S. Dymond and W. Charles Sayers were admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. William Dixon, 3, Belle Vue Park, Sunderland; Thomas Flower Ellis, Widmore, Bromley, Kent; Frederick John Hambly, 13, Osborne Place, Dundee, N.B.; Charles Terry Holloway, 188, Lewisham High Road, S.E.; John Stewart MacArthur, 46, Melville Street, Pollockshields; Harold Picton, 80, Regent's Park Road, N.W.; Alexander Smith, 4, West Castle Road, Edinburgh.

The following lecture was delivered:—

"The evidence afforded by petrographical research of the occurrence of chemical change under great pressure. By Professor J. W. Judd, F.R.S., F.G.S., &c.

The materials constituting the deeper parts of the earth's crust must sustain great *statical* pressures, due to the weight of superincumbent rock-masses; some of these materials, too, have from time to time been subjected to enormous *dynamical* pressures resulting from the stresses which arise during mountain-making and other earth-movements. Hence it is found that the rocks and minerals which have at any time formed the deeper parts of the earth's crust show many striking evidences of the action of these pressures: among these may be mentioned the cavities filled with various supersaturated solutions, carbon dioxide and other materials; there are also re-

markable indications of strain, distortion and fracture presented by the minerals when their optical properties are studied.

The question was discussed how far the phenomena observed by the geologist in his study of rocks under the microscope can be explained by the laws that have been experimentally determined by the physicist and chemist: and it was pointed out that the conclusions to which both the experiments of physicists and chemists and the observations of mineralogists and geologists point are as follows:—

1. In all those cases in which crystallisation is accompanied by *contraction*, the tendency of pressure is to promote the change from an amorphous to a crystalline condition.

2. Crystallised minerals developed in a magma under pressure may lose their stability, and be dissolved by the same magma when the pressure is removed.

3. In all those cases in which solvent action is accompanied by *contraction*, dissolution is promoted by pressure.

4. Under great statical pressures the whole substance of solid bodies may be permeated by fluids (liquids and gases alike), and chemical action between these and the solids is thus greatly facilitated.

5. By the intimate admixture, under great statical pressures, of solids with fluids, the properties of the former are remarkably modified.

6. Mechanical stresses, which tend to overcome the attraction between the particles of a solid, promote chemical action at those parts of the mass which are in a condition of intense strain.

7. Pressure may supply the conditions required for the renewal of the growth of crystals, when their development has been arrested for an indefinite period, and even after they have suffered mechanical injuries.

8. When dissolution under pressure is going on in a crystalline substance, the action is controlled and modified by its molecular structure; this structure having been produced in the process of crystallisation, or having been acquired by the crystal subsequently, owing to the action of mechanical and other forces upon it.

9. Under great pressures paramorphic changes take place in crystalline substances, without change in their chemical composition.

10. Both the dissolution of existing compounds and the formation of new crystallised minerals may result from pressure; and these two operations frequently going on together, pseudomorphs are produced, the action sometimes affecting great rock-masses.

11. When, as the result of *dynamical* pressures, the crystalline constituents of rocks are brought into close contact, chemical affinities come into play between them, and new mineral species result from

the interactions. This operation is facilitated when, as the result of internal strains, differential movements are set up in a rock-mass, and rubbing or sliding contacts between the particles are brought about.

12. When internal strains and differential movements affect a mass in which the process of crystallisation is going on, the forms and positions of the crystals may be modified. The structures known to geologists as "granulitic" and "foliated," which characterise the crystalline schists, have been produced in this way, as was shown by Scrope, Dana, Darwin, Sharpe and Naumann, and confirmed by many subsequent investigators.

In arriving at these conclusions recourse has been had only to proved causes of change, and hypothetical causes have been avoided. Some of them may seem insignificant, but, affecting, as they have done, vast masses of material during enormous periods of time, the results accomplished by such apparently insignificant causes have been very great.

Although *dynamical* pressures may be converted into heat, as shown by Mallet, or into chemical action, as argued by Sorby, no very distinct evidence of great effects having been produced by these methods has been discovered.

The following papers were read :—

21. "The formation of triazine-derivatives." By R. Meldola, F.R.S.

In consequence of a recent paper by Goldschmidt and Rosell (*B.*, 1890, 487), which to some extent anticipates an investigation upon which the author and C. Tyrer have been at work for some time, the method adopted for the synthesis of triazine-derivatives is briefly described in this communication. The method consists in acting on a benzylidene derivative of an amine with a diazo-salt so as in the first place to form an orthazo-compound; on heating a solution of the azo-compound, preferably in glacial acetic acid, the benzylidene and azo-groups then undergo condensation, forming a triazine-ring. In this way diphenyl-$x\beta$-naphthotriazine, having the formula $C_{10}H_6<\begin{matrix}N—N\cdot C_6H_5\\ |\\ N—CH\cdot C_6H_5\end{matrix}$, has been prepared from benzylidene-β-naphthylamine and diazobenzene chloride. It is a feeble base forming dense flat white needles melting at 193—194°, dissolving with difficulty in benzene and but very sparingly soluble in alcohol. Other triazine-derivatives prepared by this method are in course of investigation.

22. "Contributions to the knowledge of mucic acid. Part I. hydromuconic acid." By S. Ruhemann, Ph.D., M.A., and F. F. Blackman, B.Sc.

Chloromuconic acid, prepared from mucic acid in accordance with Bode's directions (*Annalen*, **132**, 195), is very stable, as indeed Limpricht has already stated; its chlorine is not displaced by the action of boiling alcoholic potash or ammonia; aniline acts very readily on its alcoholic solution, but the product is simply the aniline salt. Its ethylic salt is converted by ammonia into chloromuconamide.

The authors find that chloromuconic acid is most conveniently converted into hydromuconic acid by treatment with tin and chlorhydric acid. Of the two possible formulæ of this acid,

$COOH{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$ and $COOH{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}COOH$,

there can be no doubt that the former is to be regarded as correct, as v. Baeyer has shown that hydromuconic acid is obtained on reducing the dicarboxylic acid, $COOH{\cdot}C{:}C{\cdot}C{:}C{\cdot}COOH$.

It appears that, contrary to Limpricht's statement, the same dibromadipic acid is obtained by the action of bromine on hydromuconic acid when acetic acid is taken as solvent as when water is used. The acid melts at 185—207°, according to the rate of heating. Ethylic dibromadipate, prepared either directly from the acid or by brominating ethylic hydromuconate, crystallises in long needles melting at 64°; by the action of ammonia, this salt is converted into the amide of an acid isomeric with muconic acid. This *isomuconic* acid, $C_6H_6O_4$, can be easily obtained by heating ethylic dibromadipate with alcoholic potash; it crystallises in white, fine needles, very sparingly soluble in water and alcohol. The barium, lead, potassium, silver, and ethylic salts of this acid are described. On oxidation with permanganate, isomuconic acid yields oxalic and succinic acids, and there can be no doubt therefore that its formula is $COOH{\cdot}C{:}CH_2{\cdot}CH_2{\cdot}COOH$.

23. "The molecular weights of metals when in solution." By C. T. Heycock, M.A., and F. H. Neville, M.A.

In a previous communication (these Proceedings, 1889, p. 41) the authors have given a preliminary account of their observations on the effect of metals on the solifying point of tin, and they subsequently described similar experiments using sodium as the solvent (*cf. Chem. Soc. Trans.*, 1889, 666). They now give the details of the investigation of solutions in tin.

Tables of results are given, showing the effect of various proportions of the following metals:—Silver, gold, copper, nickel, sodium, palladium, magnesium, zinc, lead, cadmium, mercury, bismuth,

calcium, indium, aluminium, and antimony. Of all these metals, antimony alone behaves abnormally, producing a rise instead of a depression in the solidifying point.

An example will illustrate the method of calculating the "atomic depression." In an experiment with silver, 4·3085 grams was dissolved in 400 grams of tin, *i.e.*, $\frac{4{\cdot}3085}{108}$ of an atomic proportion; and therefore there was present per 100 atomic proportions of tin $\frac{4{\cdot}3085 \times 118 \times 100}{108 \times 400} = 1{\cdot}177$ atomic proportions of silver. The observed solidifying point of the tin was 231·68°, and of the solution 228·29°, a depression of 231·68 − 228·29 = 3·39°; hence the atomic depression was $\frac{3{\cdot}39}{0{\cdot}177} = 2{\cdot}875$.

In the majority of cases the atomic depression is a number not far removed from 3. If Raoult's generalisation be true, that the depression produced by a molecular proportion of any substance in the solidifying point of the same solvent is the same whatever the substance, it would therefore seem probable that the molecules of most metals are of the same type, M_n, where n is the number of atoms in the molecule; and if it be supposed that the molecules of, say, zinc, when dissolved in tin, are monatomic, as in the gaseous state, it would follow that n is unity in the case of many other metals. The theoretical depression calculated from Van't Hoff's formula is 3, and a similar value may be deduced from a formula suggested by Professor J. J. Thomson. In the case of aluminium, the atomic depression is so nearly half the average value that it seems probable that the molecule is diatomic. Indium resembles aluminium in producing an abnormally low depression; and it is noteworthy that the value for mercury is distinctly low: in fact, the data recorded show that there are many interesting points of difference to be noted between the various metals.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Geological and Natural History Survey of Canada. Annual Report for 1887–88, with maps. Montreal 1889.

From the Director of the Survey.

Chemistry, Inorganic and Organic, with Experiments, by C. L. Bloxam. Seventh edition. Revised and edited by J. Millar Thomson and A. G. Bloxam. London 1890. From the Publishers.

One Thousand Experiments in Chemistry, with illustrations of

Natural Phenomena and practical observations on the Manufacturing and Chemical Processes at present pursued in the successful cultivation of the Useful Arts, by C. Mackenzie. London 1821.

Treatise on various subjects of Natural and Chemical Philosophy, by J. Leslie. Edinburgh 1838.

A New Course of Chemistry, by J. Millar. London 1754.

Dictionnaire de Chymie, par M. Macquer. 4 tomes. Paris 1778.
From Hy. Bassett, Esq.

A Treatise on Chemistry, by H. E. Roscoe and C. Schorlemmer. Vol. III. Organic Chemistry. Part II. New and revised edition. London 1890. From the Authors.

Contributions from the Chemical Laboratory of Harvard College, Cambridge, U.S.A. 1887–89. From Prof. J. P. Cooke.

Annual Address of the President, Mr. Edgar Richards, delivered before the Chemical Society of Washington, January 23, 1890. Some Food Substitutes and Adulterants. Washington 1890 (Pamphlet).
From the Author.

Reports from the Laboratory of the Royal College of Physicians, Edinburgh. Edited by J. B. Tuke and G. S. Woodhead. Vol. II. Edinburgh and London 1890. From the College.

Report of the First Meeting of the Australasian Association for the Advancement of Science, held at Sydney, N.S.W., in August and September, 1888. Edited by A. Liversidge and R. Etheridge, Junr. Sydney 1889. From the Association.

II. *By Purchase.*

Ueber die neuern Gegenstände der Chymie, von J. B. Richter. Stücke 1—6 and 9. Bresslau und Hirschberg 1791–1798.

Chymische Schriften, von A. S. Marggraf. 2 Theile (zusammen gebunden). Berlin 1761–67.

Nützliche Observationen; oder Anmerkungen von den fixen und flüchtigen Saltzen, von J. Kunckel. Hamburg 1676.

Königliche hermetische Special-Concordanz, von J. Kunckel. Bresslau und Leipzig 1724.

Vollständige Glassmacherkunst; nebst einem Anhang von den Perlen und Edelsteinen, von J. Kunckel. Nürnberg 1756.

Joannis Beguini Tyrocinium chymicum, commentariis illustratum a G. Blasio. Amstelodami 1659.

Anfangsgründe der Probierkunst, von J. A. Cramer. Aus dem Lateinischen übersetzt von C. E. Gellert. Stockholm 1746.

Turba philosophorum; Das ist das Buch von der güldenen Kunst, neben anderen Autoribus welche mit einander 36 Bücher in sich haben; an Tag geben durch P. Morgenstern. Basel 1613.

Chymisch-physische Schriften, von F. C. Achard. Berlin 1710.

Anfangsgründe der antiphlogistischen Chemie, von C. Girtanner. Berlin 1792.

Oswaldi Crollii, Basilica chymica. Francofurti 1659.

Art de la vererie, de Neri, Merret, et Kunckel. Traduit par M. D. Paris 1752.

L'art de convertir le fer forgé en acier et l'art d'adoucir le fer fondu, de Réaumur. Paris 1722.

De Elia Artista, oder was Elias Artista für einer sey und was Er in der Welt reformiren oder verbesseren werde wann er kombt; von J. R. Glauber. Amsterdam 1668.

De auri tinctura, sive auro potabili vero, per J. R. Glauberum. Amsterodami 1651.

De igne secreto philosophorum, oder, Geheimen Feur der Weisen. durch J. R. Glauber. Amsterdam 1669.

Miraculum mundi, sive plena perfectaque descriptio admirabilis naturæ, a J. R. Glauber. Amsterodami 1653.

Chymische Schriften, von F. Basil Valentinus. 2 Bände. Hamburg 1694.

J. J. Becheri Experimentum novum ac curiosum de minera arenaria perpetua, sive Prodromus Historiæ. Lipsiæ 1703.

Institutiones chimicæ prodromus, i.e., J. J. Bercheri Œdipus chimicus obscuriorum terminorum et principiorum chimicorum. Francofurti 1664.

Psychosophia, oder Seelen-Weisheit, von J. J. Becher. Vierte Edition. Hamburg 1725.

Actorum Laboratorii chymici monancensis, seu physicæ subterraneæ. Libri duo, elaboravit J. J. Becherus. Francofurti 1669.

Chymischer Glücks-Hafen oder Grosse chymische Concordanz, von J. J. Becher. Franckfurt 1682.

Introduction à l'étude de la chimie des anciens et du moyen age, par M. Berthelot. Paris 1889.

Les Origines de l'alchemie, par M. Berthelot. Paris 1885.

Oel- und Buchdruckfarben, von L. E. Andés. Leipzig 1889.

March 27th. 1890. Annual General Meeting. Dr. W. J. Russell, F.R.S., President, in the Chair.

The President delivered an address, of which the following is an abstract:—

There are at present 1,733 Fellows of the Society, of whom 34 are honorary foreign members; at the same period last year there were 1,650 Fellows, including 36 honorary foreign members.

145 Fellows have been elected during the year.

16 Fellows have died during the year:—Richard Anderson, M. T. Buchanan, M. Chevreul (foreign member), John Dale, Dr. Warren de la Rue, Ernest H. Francis, Prof. A. Genther (foreign member), James Hindle, J. P. Joule, Benjamin Nickels, Henry Pollock, Owen Prosser, Dr. R. Romanes. Dr. Edmund Ronalds, Joseph Stapleton, Dr. David Waldie.

12 Fellows have withdrawn:—S. F. Burford, E. B. Clarke, N. M. Falkiner, Alex. Galt, John Innes, Alfred Neild, W. F. Pankhurst, Forbes Rickard, Newton Samuelson, Rev. S. D. Titmas, Wm. Weston, G. H. With, Charles Williams.

34 Fellows have been removed from the Society's list on account of arrears:—G. W. Arnott, A. B. Avarne, W. Alabaster, W. A. Bradbury, F. W. Drinkwater, Joseph Fletcher, F. W. Fleming, T. H. Judson, Chas. A. R. Jowett, T. N. Kirkham, John W. King, R. W. E. MacIvor, E. C. L. Muspratt, K. D. Naegamvala, W. O. Nicholson, Rev. P. R. Ogle, J. B. Orr, C. H. Piesse, A. N. Pearson, Victor E. Perez, A. E. Robinson, Alfred Southall, J. Schwarts, Frederick Sear, F. W. Simpson, J. H. Thompson, John A. Tate, Caleb Terry, John D. Veira, Peter H. Walsh, R. N. Wolfenden, H. P. White, Edward Willmore, and Chas. F. Young.

100 papers have been communicated to the Society during the session; a considerable number of these have, at their authors' request, been published in the "Proceedings," now in the sixth year of its existence, and which has become a most valuable adjunct to the Journal, serving to give as wide and as important a publicity to a paper as the "Transactions," and at the same time affording a rapidity of publication not exceeded by any other scientific journal.

In the year 1889, 71 papers, occupying 773 pages, have been published in the "Transactions;" 75 papers, occupying 895 pages, having been published in 1888. The number of abstracts published during 1889 is 2,131, which occupy 1,252 pages: the number is considerably smaller than in the previous year, when it was exceptionally large, viz., 2,470, occupying 1,351 pages.

After speaking with approval of the work done by the Publication Committee and the Editors, the President said that it was intended to give more attention in future to the abstracts of analytical papers, and to illustrate these when necessary; and referring to the fact that next year the Society will have been in existence 50 years, he said that it had been suggested that the issue of a complete subject catalogue of the Society's original publications would be a fitting memorial of the occasion; such a work was practicable, and the Society had the means of carrying it out.

Not only had the Library Committee procured a considerable

number of new books during the year, but by the generosity of several Fellows and others, and by purchase, a very important addition had been made to the Library of old books. The importance to the Society of a complete collection of historical works could not be overrated: the Committee lose no opportunity of securing such works, but they trust that Fellows will, whenever possible, assist their efforts in this direction, and he would remind them how much the value and interest of an old book is increased when it becomes an integral part of a series of historical works such as the Society already possesses. The present state of the Library shelves is shown in the following table:—

	March 31st, 1889.	Additions in 1889–90.	Present State.
Volumes of systematic works	2,922	160	3,082
Volumes of journals	5,474	193	5,667
Volumes of duplicate journals for circulation	1,084	51	1,135
Pamphlets	1,426	24	1,450
	10,906	428	11,334

The expenditure under this head during the year had been £270 18*s.* 11*d.*

During the year the Royal Society had awarded both the Davy and a Royal medal to Fellows of the Society, and he felt sure, said the President, that all rejoice that the important investigations of Dr. Perkin and of their Treasurer, Prof. Thorpe, had met with such well deserved recognition of their value.

Referring to the alteration which had been made in the time of the anniversary meeting, and to the dinner which was to take place in the evening, the President said that it had been thought that it would be of advantage to the Society in general to follow the example of other societies and to have an anniversary dinner; and it was hoped that the change would have the effect of bringing a large number of Fellows together, and that those not resident in London would feel it to be a duty as well as a pleasure to attend at least the annual evening meeting of the Society.

The recent important lecture for which the Society was indebted to Professor Judd was referred to. Attention was then drawn to the special meeting for the exhibition of apparatus to be held on May 8th next; in every active laboratory there is to be found apparatus devised to meet some special requirement which has not been made known, which can be appropriately shown at such a meeting.

The President then proceeded to discuss the teaching of chemistry to medical students. It was too seldom recognised that the fundamental action of medicines—the origin of their power—is a chemical change, and hidden and complicated as are the changes produced by medicines, they must ever retain their chemical character: if an understanding and appreciation of their effects is to be sought for, the first step must be to learn the laws which govern chemical action, and the chemical nature of the substances employed. But in addition to furnishing so many of the elementary facts on which the rational practice of medicine rests, chemists may claim that a better schooling cannot be devised for the student of medicine than that afforded by the study of these facts in their simplest form. Reference was made to the Reports of the British Association Committee on the Teaching of Chemistry in Schools, and to the influence exercised by the Science and Art Department on the teaching of chemistry throughout the country, in proof that, however imperfect the system of teaching has been, attention is now drawn to the importance of effecting an improvement, and that it is to be expected that the number of students will rapidly increase, and that the quality of the teaching will advance.

While protesting most emphatically against the exclusion of chemistry from the medical curriculum, the President said that chemists had, he thought, unduly urged an extensive knowledge of their science as necessary to the medical man; he would willingly relinquish the idea of making him a chemist, but he most pertinaciously adhered to the statement that he must be well trained in elementary chemistry. If students were encouraged to regard elementary knowlege as of no use and the methods by which knowledge is gained from experiment as of no avail to them, we should be educating them to become empiricists instead of fitting them to become observant and reasoning human beings. He thought that chemistry should be placed in the same category as the recognised subjects of general education, and made obligatory in the preliminary examination; all students on commencing their career at the medical school would then have some knowledge of the subject: the teacher there would commence his instruction at a higher level than at present, and would be able to enforce his teaching by preference by means of illustrations having a technical bias. The Examining Board of the two Colleges insists in the case of anatomy, medicine and physiology that the student shall have studied at a recognised medical school, thus recognising most wisely the importance of study under efficient instructors and at places properly equipped; he desired to protest most strenuously against the exclusion of chemistry from this healthy regulation. At present the candidate, on presenting himself for ex-

amination in chemistry, has but to produce a certificate stating that he has received chemical instruction: if only qualified persons gave certificates, these would be of value; as it is, he failed to see the use of the certificates. A strong feeling is growing up that a most valuable, if not indispensable, adjunct to examinations is the knowledge where the student has studied, and the guarantee that he not only has had proper and sufficient opportunities, but also that he has made use of them. If all restrictions be waived in the case of chemistry, and everything be allowed to depend on an examination, the examination must be made far more searching than at present, and in place of hours must last for days.

It would be of great advantage to the medical student to direct his attention to chemistry at two distinct periods; and, in addition to the elementary class, there should be in every medical school a higher class for students who have time and inclination for the more thorough study of the subject. The teacher of physiology and the teacher of chemistry should work together far more than is now the case; at present the student regards the chemistry of the chemical teacher as something distinct from and not nearly so necessary as the chemistry of the physiologist.

The Fellows of the Society could best realise the advantages to be derived from the careful and accurate study of chemistry, and it must devolve on them, while not blind to the importance of other studies, to advocate that chemistry should be assigned its proper place, and should be efficiently taught, not only to the medical student, but as a branch of a liberal and general education to all other students.

Sir F. A. Abel proposed a vote of thanks to the President, coupled with the request that he allow his address to be printed; Professor Emerson Reynolds seconded the motion; Mr. Cassall then spoke on behalf of the motion, in order to give expression to his views as to the status of Fellows of the Society. The motion was carried by acclamation. The President having acknowledged the vote,

Professor Thorpe, the Treasurer, gave an account of the financial position of the Society. The receipts by admission fees and subscriptions had been £3637; by sale of the Journal £377 3*s.*; and by dividends on invested capital £340 10*s.* 9*d.* The expenses on account of the Journal had been £2310 18*s.* 3*d.*; on account of the Proceedings, £177 4*s.* 7*d.*; on account of the Library, £420 8*s.* 11*d.*: the total expenditure being £3578 18*s.* 8*d.* £530 had been invested in Metropolitan Board of Works 3½ per cent. stock, and the balance in hand was £2036 2*s.* 7*d.*, as against £1833 13*s.* 6*d.* at the corresponding period last year.

Dr. H. Müller proposed that the thanks of the Fellows be tendered

to the Treasurer for his services during the past year; the motion was seconded by Professor Dunstan. Professor Thorpe, after replying, proposed a vote of thanks to the Auditors, Messrs. R. H. Davies, Bernard Dyer and R. J. Friswell; this was seconded by Mr. F. J. M. Page and acknowledged by Mr. Davies.

A vote of thanks to the Officers and Council, having been proposed by Mr. Carteighe and seconded by Professor Ramsay, was acknowledged by Professor Thomson.

Mr. Warington moved that thanks be tendered to the Editors, Abstractors and Librarian; Mr. Pickering seconded the motion; Mr. Groves replied.

Mr. T. Fairley and Mr. Wm. Thorp having been appointed scrutators, a ballot was taken, and as result the following were declared elected as Officers and Council for the ensuing session:—

President: W. J. Russell, Ph.D., F.R.S.

Vice-Presidents who have filled the office of President: Sir F. A. Abel, C.B., D.C.L., F.R.S.; W. Crookes, F.R.S.; E. Frankland, D.C.L., F.R.S.; J. H. Gilbert, Ph.D., F.R.S.; J. H. Gladstone, Ph.D., F.R.S.; A. W. Hofmann, D.C.L., F.R.S.; H. Müller, Ph.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, Ph.D., F.R.S.; Sir Lyon Playfair, Ph.D., K.C.B., F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents: Dr. A. Crum Brown, F.R.S.; G. Carey Foster, F.R.S.; W. N. Hartley, F.R.S.; J. W. Mallet, M.D., F.R.S.; J. Emerson Reynolds, M.D., F.R.S.; Robert Warington, F.R.S.

Secretaries: H. E. Armstrong, Ph.D., F.R.S.; J. Millar Thomson, F.R.S.E.

Foreign Secretary: F. R. Japp, LL.D., F.R.S.

Treasurer: T. E. Thorpe, B.Sc., F.R.S.

Ordinary Members of Council: Henry Bassett; Norman Collie, Ph.D.; C. F. Cross; Wyndham Dunstan; John Ferguson, M.A.; E. Kinch; Raphael Meldola, F.R.S.; M. M. P. Muir; F. J. M. Page; S. U. Pickering, M.A.; R. T. Plimpton, Ph.D.; Thomas Purdie, B.Sc.

First Anniversary Dinner. Thursday, March 27th, 1890. Dr. W. J. Russell, F.R.S., President, in the chair.

Whitehall Rooms, Hôtel Métropole, 7.30 P.M.

The following were present:—

Abel, Sir F. A.
Allen, A. H.
Anderson, W.
Armstrong, Dr. H. E.
Atkinson, Dr. E.
Attfield, Prof.
Austen, Prof. W. Roberts.

Bauerman, H.
Bassett, H.
Bayly, F. W.
Beale, W. P.
Bechler, M.
Bell, Sir Lowthian.
Bell, W. J.
Best, E.
Bevan, E. J.
Blount, B.
Blundstone, E.R.
Borns, Dr. H.
Braham, P.
Bramwell, Sir F.
Brough, B.
Brunton, Dr. Lauder.
Buchanan, J. Y.

Carpmael, A.
Cooper, A.
Crookes, W.
Cross, C. F.

Davies, R.H.
Dewar, Prof. J.
Dixon, W. H.
Down, F.
Drapers' Company, Master of the.
Dunstan, Prof. W. R.
Dyer, Thiselton.

Ekin, C.

Fairley, T.
Foster, Prof. G. C.
Foster, Prof. M.
Foster, W.
Francis, G. B.

Gilbert, Prof. J. H.
Gladstone, Dr. J. H.
Godson, M. C.
Gordon, J. G.
Green, Friese.
Greenaway, A. J.
Groves, C. E.

Harrison, R.
Harley, Dr. G.
Harris, E. S.
Hills, W.
Hofmann, Herr V.
Howard. D.
Howie, W. L.
Hummel, Prof. J. J.

Ince, Dr. W.
Institute of Chemistry, President of the.
Institute of Electrical Engineers, President of the.

Japp, Dr. F. R.
Judd, Prof.

Kellner, Dr. W.

Laws, J. P.
Lawson, T. A.
Lyon, J. B.

Matthey, Edward.
MacEwen, P.
McNeil, B.
Mellin, G.
Merz, Dr.
Moody, Dr. G. T.
Moritz, Dr. E. R.
Moul, F.
Müller, Dr. H.

Naylor, W.
Newton, W.

Odling, Prof. W.

Page, J. F.
Parsons, P. R.
Paul, Dr. B.
Pharmaceutical Society, President of the.
Physical Society, President of the.
Pickering, S. U.
Pilley, J. J.
Prentice, M.
Prideaux, W.
Pullar, Dr. A.
Pullar, R. D.
Pyke, L. O. M.

Ramsay, Prof. W.
Reynolds, Prof. E.
Roberts, Sir Owen.
Roscoe, Sir H.

Royal Society, President of the.
Ruhemann, Dr.

Salamon, A. G.
Sellon, J. H.
Senier, Dr.
Smith, H. R.
Smith, F.
Smithells, Prof. A.
Stewart, C. W.

Thorne, Dr. L.
Thorp, W.
Thorpe, Prof. T. E.
Thomson, Prof. J. M.
Tidy, Dr.
Tilden, Prof. W. A.
Tookey, C.

Voeleker, E. W.

Warington, R.
White, Rev. Henry.
Williams, W. M.
Wynne, W. P.

The following toasts were proposed:—

By the President.

1. Her Most Gracious Majesty the Queen.
2. Their Royal Highnesses the Prince and Princess of Wales and the rest of the Royal Family.
3. Prosperity to the Chemical Society.

By Sir F. A. Abel, C.B., F.R.S.

4. Kindred Societies and Institutions, coupled with the names of Sir Gabriel Stokes, M.P., Pres. R.S., and Sir Lowthian Bell, F.R.S.

By Professor M. Foster, Sec. R.S.

5. The Visitors, coupled with the names of the Honorary Secretary of the Royal Institution and the Director of the Royal Gardens, Kew.

By Sir Henry Roscoe, M.P., F.R.S.

6. The President.

By Professor Odling, F.R.S.

7. The Officers, coupled with the name of Dr. Armstrong.

HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY, ST. MARTIN'S LANE.

Issued 14/4/1890.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 81. Session 1890–91.

April 3rd, 1890. Dr. Hugo Müller, F.R.S., Vice-President, in the Chair.

Certificates were read for the first time in favour of Messrs. James Robert Appleyard, University College, Dundee; William Henry Blake, 31, Norfolk Street, Sunderland; George Caird, 20, Springfield, Dundee; S. Sydney Monckton Copeman, M.A., M.B. Cantab. 134, York Road, S.E.; Andrew Fairgreve, Sydney, New South Wales; G. H. Findlay, Hawthorn Cottage, Francis Road, Edgbaston, Birmingham; George German, Junior, Huntingdon House, Ashby de-la-Zouch; John Archyll Jones, 3, Jedburgh Street, Middlesbrough; Oliver Kirk, Science Schools, South Kensington; Robert Waller Oddy, Waterhouse, Toad Lane, Rochdale.

The following papers were read:—

24. "Note on the hydrosulphides." By S. E. Linder and Harold Picton.

The authors find that freshly precipitated metallic sulphides almost always contain hydrogen sulphide: that they are, in fact, hydrosulphides, or the remnants of hydrosulphides; and that if, instead of adopting the usual plan of passing gas through the solution, the metallic salt be allowed to run slowly into a solution of hydrogen sulphide in water, in absence of too large an excess of acid, a solution is obtained which can in most cases be freed from dissolved hydrogen sulphide by a current of hydrogen, although this to some extent depends on the character of the acid liberated from the salt. The solutions so obtained are readily precipitated by the addition of metallic salts, a fact long made use of in washing a sulphide such as

that of tin, in which case the addition of sodium chloride to the water is always advised.

A large number of experiments on the formation and properties of the metallic hydrosulphides have been made, and, although the work is not yet completed, it is thought to be desirable to indicate generally, and with the aid of two typical examples, the character of the results obtained.

To prepare the higher hydrosulphides, it is found to be necessary to avoid the presence of acid. An unexpected method of accomplishing this has presented itself in certain cases: in that of mercury, for example. If carefully washed mercuric sulphide be treated with hydrogen sulphide and water, it dissolves to a clear brown solution from which uncombined hydrogen sulphide may be removed by a current of hydrogen. Another method which it is hoped will be generally applicable is the treatment of the metallic hydroxides with hydrogen sulphide. Precipitation with sodium hydrosulphide or ammonium hydrosulphide may be resorted to in some cases. By whatever method they are prepared, the hydrosulphides are probably in all cases compounds of high molecular weight. The effect of acids on their formation and constitution is of much interest, as these apparently cause a molecular condensation and increase of complexity, which becomes more marked as the acids become more powerful. Variation in temperature does not appear to exercise any important influence.

The sulphur in the hydrosulphide has been determined as sulphate after oxidation with chlorine, great care having been taken to avoid the precipitation of sulphur during the formation of the sulphide; to make assurance on this matter doubly sure, the authors have in some cases heated the carefully washed sulphate in a current of hydrogen freed from every trace of hydrogen sulphide, the hydrogen sulphide lost on heating being absorbed by potash and oxidised. This method is of special importance as affording confirmation when the combined hydrogen sulphide, as in the case of mercury, is very small in amount.

Copper.—On treating copper hydrate suspended in water with hydrogen sulphide, the hydrosulphide $7CuS{\cdot}H_2S$ is rapidly formed, and if left for some days in a tightly stoppered vessel dissolves to a clear brown solution. The effect is the same whether time be given for the solution to form or not. Three results differing from the mean by only about 0·07 in the percentage of sulphur gave as a mean 36·69 per cent. of sulphur, the amount calculated for $7CuS{\cdot}H_2S$ being 36·59 per cent.

In order to prevent the liberation of sulphuric acid during the interaction, sodic acetate was added to the copper sulphate, and the solution formed by adding the mixture to water saturated with

hydrogen sulphide was precipitated with ammonic chloride: 2 molecular proportions of acetic acid were present for each molecular proportion of CuS. In this case the acetic acid acts in presence of excess of hydrogen sulphide, and has but little effect in breaking down the hydrosulphide. The percentage of sulphur found was 36·00; that calculated for $9CuS{\cdot}H_2S$ is 35·96 per cent.

In two experiments in which some acetic acid was present at starting a precipitate was gradually deposited, which was filtered off without adding salt; great difficulty was experienced in effecting filtration owing to the fine state of division of the sulphide. Slightly higher numbers were obtained, probably owing to the deposition of some sulphur, but they serve to indicate that the salt does not alter the composition of the precipitate; the percentages of sulphur found were (1) 36·13, (2) 36·28.

In another case, after adding sodic acetate, the excess of hydrogen sulphide was expelled from the solution of the hydrosulphide by hydrogen. The acetic acid was thus allowed to act upon the solution unsaturated with hydric sulphide. The percentage of sulphur found was 34·67 and 34·56; that calculated for $22\ CuS{\cdot}H_2S$ is 34·61.

In this case the excess of sulphur is very small, and it is impossible to assign a formula; it is noticeable that a great molecular condensation has taken place.

In presence of hydrogen chloride, still further loss of sulphuretted hydrogen occurs. All the filtrations were conducted in an atmosphere of hydrogen.

Mercury.—Solutions of two similar quantities of mercuric chloride were taken; after boiling to expel air, one was run into boiled water containing hydrogen sulphide placed in a Drechsel's bottle, access of air being prevented by a current of the gas: the mixture was precipitated by hydrogen chloride. The other, after dilution with boiled water, was made acid and precipitated by hydrogen sulphide. Both precipitates were washed with boiled water, then mixed with boiled water in a Drechsel bottle, and hydrogen sulphide was passed into the liquid till clear solutions were formed. A current of hydrogen was then passed through both, the one being cooled with ice, till they were free from hydrogen sulphide. The amount of barium sulphate obtained from A was 0·8910, from B 0·8916; the amount afforded by the same weight of mercuric sulphide is 0·86375. The mean percentage of sulphur found was 14·166; a compound of the formula $31HgS{\cdot}H_2S$ would contain 14·171 per cent.

In presence of hydrogen chloride a further molecular condensation takes place, the quantity of attached hydrogen sulphide becoming apparently halved; it is of course impossible to assign an exact formula to a product of so high a molecular weight, but the concordance of the results

and its very remarkable stability would make it probable that the compound is a definite one. It withstood extraction with carbon disulphide, and the prolonged washing which this entailed. It did not lose its hydrogen sulphide *in vacuo*, and after drying *in vacuo* it required to be heated for about 16 hours at 105° in a current of hydrogen before all the hydrogen sulphide was removed. The dryness of the hydrosulphide seems to greatly influence the rapidity with which it loses hydrogen sulphide.

25. "Researches on the germination of some of the Gramineæ." Part I. By Horace T. Brown, F.R.S., and G. Harris Morris, Ph.D.

This investigation was undertaken with the view of throwing some light upon the complex metabolic processes which take place during the germination of seeds. The authors during the progress of the inquiry have examined and experimented with the seeds of a great number of the grasses, but this, the first part of their paper, is confined almost entirely to a consideration of the changes which take place in *barley* during the early periods of its growth.

The paper is divided into 21 sections, the heads of which are as follows :—

(1.) Introduction. (2.) Structure of a grain of barley. (3.) The visible changes which occur in the embryo and endosperm during germination. (4.) The relation of the embryo to the endosperm. (5.) Development of excised embryos upon foreign endosperms. (6.) The endosperm to be regarded as a storehouse of *dead* reserve material; no residue of vitality recognisable in its cells. (7.) Cultivation of excised embryos upon water. (8.) Cultivation of excised embryos upon nutrient solutions. (9.) Growth of excised embryos upon *starch*, and proof that an amylo-hydrolyst (diastase) is secreted by the growing embryo. (10.) The secretion of diastase is localised in the "absorptive epithelium." (11.) The secretion of diastase is increased by the presence of a small quantity of acid. (12.) The secretion of diastase not stimulated by the presence of starch. (13.) The secretion of diastase is inhibited by a readily assimilable carbohydrate. (14.) The existence of a *cellulose-dissolving* enzyme (cyto-hydrolyst) in the germinating seeds of the grasses. (15.) The cyto-hydrolyst, like diastase, is secreted by the "absorptive epithelium." (16.) The two varieties of diastase, their genesis and distribution in the resting and germinating seed. (17.) Distribution of diastase in the germinating seed. (18.) The "mother-substance" of the "diastase of secretion" is principally derived from the endosperm. (19.) Action of "diastase of secretion" upon ungelatinised starch. (20.) A consideration of the origin of the hydrolytic enzymes of ger-

minated grain. (21.) The form in which the reserve starch after transformation enters the growing embryo, and the metabolic changes which it there undergoes.

In recording the visible changes which occur in the seed during germination, it is shown that a disintegration and dissolution of the cell-walls of the endosperm always precede any attack upon the cell contents. This breaking down of the cell-wall is shown in a subsequent portion of the paper to depend on the production during germination of a special cellulose-dissolving or "cyto-hydrolytic enzyme," which, like diastase, is soluble. The action of this enzyme on the cell-walls of some kinds of vegetable parenchyma is very energetic. The physiological importance of this cyto-hydrolyst is very great, for, owing to the non-diffusible nature of the amylo-hydrolytic enzyme, diastase, the previous breaking down of the cell-wall is a necessary prelude to the dissolution of the contained starch-granules.

The authors show that the appearance of the cyto- and amylo-hydrolysts is due to a specialised secretory function of the layer of columnar epithelium which covers the outer surface of the scutellum. It has hitherto been considered that the function of this epithelium was exclusively that of an absorptive tissue: its absorptive as compared with its secretory functions are, however, of quite secondary importance.

The natural food material, *starch*, does not appear to have any special power of stimulating the cells of the epithelium to increased secretion of a diastase, but the flow both of diastase and of the cyto-hydrolytic enzyme from these cells is affected in a very remarkable manner by the presence of certain carbohydrates. Providing the carbohydrate is one which is readily assimilable by the embryo, such as cane-sugar or maltose, secretion of ferment is checked or even entirely inhibited. No such inhibitory action is, however, produced by such substances as mannitol and milk-sugar, which are entirely without nutritive value. The authors' experiments in this direction point to the secretion of the amylo-hydrolytic and cyto-hydrolytic enzymes as being to some extent *starvation phenomena*. The power of secretion possessed by the epithelium is in some way or other so adapted to the requirements of the young plant as to be only exercised when the supply of tissue-forming carbon compounds begins to fail.

The histological changes which take place in the cells of the epithelium during secretion are very similar to those which have been observed in certain secretory cells of the alimentary tract of animals, and in the secretory cells of some of the insectivorous plants.

The authors confirm the important generalisation of Sachs that the relation of the embryo to the endosperm is that of parasite to host, and they have availed themselves of this relation by cultivating

the embryo upon suitable media after separating it from its endosperm, and in this way they have obtained information with regard to the secretory powers of the embryo, and the chemical modifications of its absorbed nutriment, which it would have been impossible to obtain by any other means.

The results of cultivating excised embryos upon various nutrient solutions, more especially of the carbohydrates, are recorded, and it is shown that whilst cane-sugar, invert-sugar, dextrose, lævulose, maltose, raffinose, galactose and glycerol have all more or less nutrient value, milk-sugar and mannitol do not in any way contribute to the growth of tissue in the young plant. Of all substances tried, cane-sugar has by far the greatest nutritive power. Maltose, although the natural food of the embryo when attached to its endosperm, is decidedly inferior in this respect to cane-sugar. This, at a later point in the paper, is shown to be due to the fact that maltose, directly it is absorbed by the growing embryo, becomes transformed into cane-sugar by the living cells, and in this form is passed from cell to cell. When cane-sugar is supplied ready formed to the young plantlet, there is manifestly a saving of energy to the living cell, which receives its nutriment in a form in which it is directly available for its requirements.

An examination of the sugars produced during the germination, and of their mode of distribution in the grain, have convinced the authors that the transformed starch of the endosperm is absorbed by the embryo in the form of maltose, and that the seat of production of the cane-sugar which germinated grain contains is the tissues of the embryo itself.

The authors are continuing their work upon the germination of the grasses, and are applying the methods described in this first part of their paper to an elucidation of the chemical changes which the other reserve materials, especially the proteids, undergo in their passage from the endosperm, and of the agencies which are at work in bringing about these transformations.

Discussion.

Mr. Thiselton Dyer said that chemists, perhaps, would hardly realise what delicacy of manipulation was required in carrying out experiments such as had been instituted by the authors of the paper; it was a fortunate circumstance that the morphology of the seed in grasses allows of anatomical separation of the elements. Botanists had already made some progress in localising enzymes: thus Professor Marshall Ward had shown that the enzyme which effects the liberation of the colouring matter from the gluco-side in Persian berries is

located in the raphe; and it had long been known that emulsin was not distributed throughout the bitter almond. After referring to the distinction between animals and plants, he said that the plant was similar to the seed, the bud corresponding to the embryo and the woody shoot to the endosperm. Baranetzky had shown that a diastase is omnipresent in plants; and there could be little doubt that it would be found that an enzyme capable of attacking cellulose was equally so.

Professor Marshall Ward pointed out that in the seeds of the Gramineæ, Cyperaceæ and other families of plants there is a peculiar layer of cells, from one to three or more deep, surrounding the starchy endosperm, and distinguished from the latter by containing no starch but relatively large quantities of proteids: this layer belongs to the endosperm, but as the seed ripens the cells store special proteids instead of the starch-grains which predominate in the other endosperm cells. In the oat there is such a layer, one cell deep, and it has been shown that, during germination, the dissolution of the starch and the cell-walls of the starch-containing cells begins near the surface of this layer, which itself persists, and the cells of which take up food and undergo changes so like those of excreting cells that it was concluded that they excrete the diastatic enzyme. Haberlandt declares that when starch-grains are placed in contact with a piece of this layer kept moist and at proper temperatures, the grains even of the resistent potato-starch are corroded as on germination; whereas control experiments, where all conditions are the same except the presence of the cells of the proteid layer, showed no such corrosion.

Professor Ward then remarked that the authors' suggestion that more than one enzyme may be excreted according to the nutrition of the cells, and their proof that a cellulose-dissolving enzyme exists in barley, is borne out by various recent researches and by Wortmann's observations on the behaviour of bacteria in a mixture of starch and proteids. Wortmann proved that so long as the bacteria were fed with proteids, they refused to excrete the diastatic enzyme which they produce in abundance when only carbohydrates are at their disposal.

The speaker concluded by drawing attention to several other cases where such a proteid layer exists—*e.g.*, in the seeds of buckwheat and in the tubers of some potatoes—and remarked on the importance of clearing up this matter, and on the steps towards accomplishing that end attained by the excellent work of the authors of the present paper.

Professor Green said that in the case of the date stone his observations led him to believe that the enzyme was independent of

the endosperm, and that probably it was located in the epithelial layer. But in castor oil seeds not only the embryo but also the endosperm cells appeared to be possessed of vitality, the fatty matter in the latter undergoing change even when not subject to the action of the embryo; probably the enzyme was present in the form of an enzymogen, as extracts of the seeds were rendered active by acids.

Dr. Lauder Brunton said that it was highly remarkable that in a comparatively highly organised plant the conditions of the embryo was so very similar to that of the embryo in animals: the embryo in both cases appeared to be purely parasitic. In the mammalian embryo proteids are taken up from without, and it is generally assumed that they are assimilated without undergoing much change, but this was by no means certain. Referring to the presence in malt of an enzyme capable of affecting cellulose, he said there was a form of indigestion in which people could not digest cellulose: was it possible to separate the enzyme in question in large quantities?

Dr. Armstrong remarked that many of the results brought forward were highly suggestive from a chemical point of view. The authors came to the conclusion that maltose, which on *a priori* grounds might be regarded as the natural nutriment of a plant, was inferior to cane-sugar, and that in the plant maltose was converted into cane-sugar. Dextrose, according to their observations, did not undergo conversion into cane-sugar, but it gave invert-sugar: that is to say, it became partially converted into lævulose, but these constituents of cane-sugar were apparently incapable of interacting. It was known from Emil Fischer's experiments that dextrose could be converted into lævulose, and that maltose was an etheric compound of the acetal type, formed from two molecules of dextrose, one of which acted as aldehyde, the other as alcohol; it was conceivable that if the "dextrose residue" in maltose underwent a change comparable with that which is involved in the conversion of dextrose into lævulose, a compound would be obtained which, if not identical with cane-sugar, would, perhaps, be easily convertible into cane-sugar by hydration and subsequent dehydration: it is scarcely probable that the keto-group—or its equivalent—of lævulose is preserved in cane-sugar, but if this group were to become $C(OH)_2$ and one of the hydroxyls were to be separated together with an atom of hydrogen of a hydroxyl-group in the other dextrose residue, a more stable etheric compound might result, the properties of which, probably, would be such as are characteristic of cane-sugar. The authors had spoken of the maltose becoming incorporated with the protoplasm, from which the cane-sugar was then elaborated; perhaps the effect was comparable with that exercised by phenylhydrazine in effecting the conversion of dextrose into lævulose through the agency of the osazone.

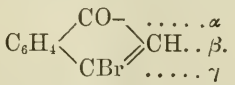
Dr. Armstrong then took exception to the terms amylolytic, proteolytic, &c., as applied to so-called ferments, pointing out that, whereas the terms electrolysis and hydrolysis implied splitting up *by means of* electricity and water, amylolytic was intended to suggest the splitting up of starch, proteolytic the splitting of proteids. He suggested several expressions less open to objection.

Mr. Heron, referring to the author's conclusion that maltose was not resolved into dextrose during germination, asked how, if this were the case, it was possible to account for the presence of dextrose in malt; he was of opinion that maize diastase did hydrolyse maltose.

Mr. Horace Brown said that although, as Mr. Thiselton Dyer had pointed out, diastase was ubiquitous in plants, that developed during germination appeared to differ in important particulars from ordinary diastase. He had been unsuccessful in isolating an enzyme capable of attacking cellulose from the date stone. Their experiments did not favour the conclusion that the cellulose layer had any marked diastatic power. He might point out that Professor Marshall Ward had been led to a conclusion similar to their own in the case of the cyto-hydrolytic enzyme which he had studied, viz., that its secretion was a starvation phenomenon. All their experiments to determine whether the enzyme existed in the endosperm as an enzymogen had been futile. In preparing the cyto-hydrolytic enzyme from malt, it was necessary to use air-dried malt, as it was destroyed by heating. In his experience there was no marked excess of dextrose in malt.

26. "The formation of indene-derivatives from dibromalphanaphthol." By R. Meldola, F.R.S., and F. Hughes.

On adding dibrom-α-naphthol to strong nitric acid (1·42 sp. gr.), an oily liquid is first formed, which subsequently solidifies to a mass of crystals, probably consisting of an additive product. If cold fuming nitric acid be used (1·5 sp. gr.), the dibrom-α-naphthol at once dissolves without any evolution of gas, and on pouring the acid solution into water an ochreous precipitate is produced, which when purified forms small ochreous scales melting at 127—128°. The substance is regarded by the authors as γ-brom-α-indone,



This compound is converted by the action of aniline into an anilide crystallising in bright red scales melting at 190°. This anilide is acid in character, dissolving in hot aqueous or cold alcoholic soda with a violet colour. The authors consider the

formula of the anilide to be $C_6H_4<\begin{matrix}C(OH)\\ |\\ CBr\ -\end{matrix}>C{:}N{\cdot}C_6H_5$. By boiling with dilute alkali, the anilide is converted into the bromhydroxyindone, $C_6H_4<\begin{matrix}C(OH)\\ |\\ CBr\ -\end{matrix}>CO$. This latter forms dull orange needles melting at 191°. During the decomposition of the anilide, a strong odour of phenyl isocyanide is evolved. The barium salt of the bromhydroxyindone forms orange needles of the formula $(C_9H_4BrO_2)_2Ba,7H_2O$. The aniline salt forms red scales melting at 169°, and decomposing at 172°. Other derivatives of the bromindone, viz., the benzylamide (m. p. 154°) and β-naphthylamide (m. p. about 151°) have been prepared. The authors propose to continue the investigation of these indene-derivatives.

27. "The action of chlorhydric acid on manganese dioxide. Manganese tetrachloride." By H. M. Vernon.

In 1821, Forchammer showed that when the oxides of manganese MnO_2, Mn_2O_3 and Mn_3O_4 are dissolved in chlorhydric acid, a dark brown solution is formed, which affords a precipitate consisting of a mixture of oxides of manganese when added to a large quantity of water. W. W. Fisher (*Chem. Soc. Trans.*, 1878, 409) showed that this brown solution contained a higher chloride of manganese, probably the tetrachloride; but S. U. Pickering (*Chem. Soc. Trans.*, 1879, 654) subsequently contended that this higher chloride was Mn_2Cl_6, his arguments being that when manganese dioxide is dissolved in chlorhydric acid and the solution is poured into water, the amount of dioxide in the precipitate is never more than about 47 per cent. of the amount originally used. According to this observer, when the dioxide is dissolved in chlorhydric acid, manganese sesquichloride is formed, two atomic proportions of chlorine being liberated; when, however, the dissolution of the dioxide is performed in the presence of manganous chloride, the amount of dioxide recovered on precipitation by water is largely increased, this increase being in a greater proportion up to the addition of one molecule of $MnCl_2$, and, hence, it would seem to show that this chloride combines with the two atoms of chlorine set free on the dissolution of the dioxide in the acid to form another molecule of Mn_2Cl_6.

In the present paper, the author shows that when manganese dioxide is dissolved in chlorhydric acid even at ordinary temperatures, of the total amount of chlorine which on Pickering's supposition should be evolved almost immediately, less than half is evolved even in the course of five hours; at −18° chlorine is evolved much more slowly, and at −26° C. only 0·35 per cent. of the available chlorine was found

to be evolved when air was drawn through the solution during two hours. That this could not be due to the formation in the solution of a solid chlorine hydrate would appear to follow from the observation that no such substance was formed when pure chlorhydric acid was saturated with chlorine at −26° C. It must, therefore, be supposed that the original product of the action of chlorhydric acid on manganese dioxide is the tetrachloride, and that no chlorine is at first formed.

In order to ascertain whether, when the tetrachloride of manganese decomposes, an intermediate chloride such as Mn_2Cl_6 is formed, weighed quantities of the dioxide were introduced into the bulb of a Victor Meyer's apparatus surrounded by a bath of water at temperatures varying from 38° C. to 63° C., and known volumes of chlorhydric acid were poured in; the volume of air expelled by the chlorine was measured at half-minute intervals. When the results thus obtained were represented in the form of curves of which the ordinates represented the volumes of gas evolved and the abscissæ the time, it was found that the curves were perfectly regular; this could not be the case if an intermediate chloride such as Mn_2Cl_6, more stable than the original tetrachloride, were formed in the solution. The curves expressing the rate of evolution of chlorine from solutions of Mn_2O_3 and Mn_3O_4 in chlorhydric acid were also perfectly regular, which shows that in the one case no chloride such as Mn_3Cl_8 intermediate between Mn_2Cl_6 and Mn_3Cl_8 was formed, and in the other case that no chloride such as Mn_4Cl_{10} intermediate between Mn_3Cl_8 and $MnCl_2$ was formed. These curves, therefore, show that on dissolving any of the oxides of manganese: MnO_2, Mn_2O_3 and Mn_3O_4, the only higher chloride formed is $MnCl_4$.

It was also found, contrary to Pickering's statement, that the amount of MnO_2 recovered on precipitating the solution was not always under but always over 50 per cent. at ordinary temperatures, the amount recovered being increased by performing the dissolution of the dioxide in chlorhydric acid saturated with chlorine. The fact that the addition of $MnCl_2$ to the solution increases the amount of MnO_2 recovered is only what we should expect, just as Wurtz found that PCl_5 dissociated to a less extent when vaporised in PCl_3 vapour.

SPECIAL MEETING, MAY 8th.

Fellows who desire to exhibit objects at the Special Meeting in May are requested to communicate *forthwith* with the Secretaries, in order to give time for the preparation of a descriptive list of the exhibits.

At the next meeting, on April 17th, there will be a ballot for the following candidates :—

1. Barker, Joseph, 8, St. James's Street, S.W.
2. Beck, Charles Ridgeway, 181, High Street, Burton-on-Trent.
3. Corrie David, Nobel's Explosives Co., Polmont Station, Scotland.
4. Dixon, William, 3, Belle Vue Park, Sunderland.
5. Ellis, Thomas Flower, Widmore, Bromley, Kent.
6. Hambly, Frederick John, 13, Osborne Place, Dundee, N.B.
7. Holburn, Andrew Cowan, B.Sc., C.E., 10, West Garden Street, Glasgow.
8. Holloway, Charles Terry, 188, Lewisham High Road, S.E.
9. Laycock, William Frederick, PhD., 2, Park Street, Dewsbury.
10. Lea, Arthur Sheridan, Caius College, Cambridge.
11. Lescher, Herman, 61, Egerton Gardens, S. Kensington.
12. MacArthur, John Stewart, 46, Melville Street, Pollokshields.
13. Mosenthal, Henry de, 220, Winchester House, Old Broad Street, E.C.
14. Müller, George, Ph.B., 125, Mercer Street, Jersey City, N. Jersey, U.S.A.
15. Neville, E. H., M.A. Cambridge, Sidney College, Cambridge.
16. Picton, Harold, 80, Regent's Park Road, N.W.
17. Scott, Ernest George, Mayer Hall, Behington, near Birkenhead.
18. Sibun, James, 2, Lax Terrace, Norton, Stockton-on-Tees.
19. Smith, Alexander, 4, West Castle Road, Edinburgh.
20. Shuttlewood, Willis Brewin, Hong Kong.
21. Stone, Frederick Richard M., 64, Thomas Street, Merthyr.
22. Walker, James S. H., 304, Morningside Road, Edinburgh.

The following papers will be read :—

"Phosphorous oxide." By Professor Thorpe, F.R.S., and Mr. A. E. Tutton.

"The action of chlorine on water in the light, and on the action of light on certain chlorine acids ;"

"the action of light on phosphorus, and on some of the properties of amorphous phosphorus ;"

"note on the explosion of hydrogen sulphide and of the vapour of carbon bisulphide admixed with air or oxygen." By Professor A. Pedler.

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Issued 23/4/1890.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 82. Session 1890–91.

April 17th, 1890. Dr. W. J. Russell, F.R.S., President, in the Chair.

Messrs. Fred. A. Anderson, Henry H. Bunting, P. A. Cobbold and D. S. MacNair were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. James Kear Colwell, 2, Lloyd Street, Lloyd Square, W.C.; William Tait, 115, Rylston Road, Fulham, S.W.

The following were elected Fellows of the Society :—Joseph Barker, Charles Ridgeway Beck, David Corrie, William Dixon, Thomas Flower Ellis, Frederick John Hambly, Andrew Cowan Holburn, B.Sc., C.E., William Frederick Laycock, Ph.D., Arthur Sheridan Lea, Herman Lescher, John Stewart MacArthur, Henry de Mosenthal, George Müller, Ph.B., E. H. Neville, M.A. Camb., Harold Picton, Ernest George Scott, James Sibun, Alexander Smith, Willis Brewin Shuttlewood, Frederick Richard M. Stone, James S. H. Walker.

The following papers were read :—

28. "Phosphorous oxide." Part I. By T. E. Thorpe, F.R.S., and A. E Tutton.

The authors describe a method of making phosphorous oxide in quantity by burning phosphorus in air. Pure phosphorous oxide melts at 22·5°, and solidifies at 21°. It boils unchanged in an atmosphere of nitrogen or carbon dioxide at 173°. Vapour-density determinations made by Hofmann's method show that its molecular weight corresponds to the formula P_4O_6. In this respect it is analogous to

arsenious and antimonious oxides, which are respectively represented by the formulæ As_4O_6 and Sb_4O_6. A determination of the molecular weight by Raoult's method, using benzene, which has no chemical action on the substance, as a solvent, also indicated the formula P_4O_6.

On heating phosphorous oxide to about 300°, it is decomposed, and at 440° it is wholly changed into phosphorus and phosphorus tetroxide, $2P_4O_6 = 3P_2O_4 + 2P$. Phosphorous oxide is readily acted on by light, and in bright sunshine its colour rapidly becomes yellow and eventually dark-red. Observations by Captain Abney show that the violet rays are most active in effecting the change. Curves showing the results of the photometric observations are given in the paper.

As first prepared, phosphorous oxide is obtained in minute crystals, aggregated into a snow-like mass. On allowing the melted oxide to cool, it solidifies in the form of thin prisms capped by pyramids; the crystals frequently attain the length of an inch or more.

The crystals appear to belong to the monoclinic system, and exhibit the pinacoidal faces $a = \{100\}\infty\breve{P}\infty$ and $b = \{010\}\infty\breve{P}\infty$, several prism faces, a pair of orthodomes and a pair of complementary pyramidal faces. The extinctions upon a are parallel to the prism edges, whilst those upon b make an angle of about 20° with the prism edges. When the crossed Nicols are parallel to the orthopinacoidal edges, the brush passes across the centre of the field in a line parallel to the vertical axis. The optic axial plane, therefore, appears to be the symmetry plane b. The crystallographical relations of P_4O_6, As_4O_6 and Sb_4O_6 are discussed in the paper.

The relative density of liquid phosphorous oxide was found to be 1·9358 at $\frac{24 \cdot 8}{4}$. Its thermal expansion, as determined by dilatometrical measurements, is expressed by the formula $V = 1 + 0{\cdot}0_391377t - 0{\cdot}0_611175t^2 + 0{\cdot}0_838607t^3$.

Its relative density at the boiling point is found to be 1·6859, whence its specific volume is 130·5. The bearing of this observation on the question of the constitution of phosphorous oxide and on the question of the varying specific volume of combined phosphorus is then discussed. Previous observations by one of the authors had shown that the specific volume of combined phosphorus is about 25. From the observations of Pisati and De Franchis and of Ramsay and Masson, the specific volume of free phosphorus is found to be about 20·9. If all the oxygen in phosphorous oxide be considered as single linked, or, in other words, to have the specific volume 7·8, the specific volume of the phosphorus in phosphorous oxide is 20·9, agreeing with the observations of Ramsay and Masson.

The conclusion to which the authors come is that, whilst the variation in the specific volume of phosphorus may be related to the atomic arrangement of the phosphorus atoms in the molecule of the element and in that of the phosphorous oxide, both of which contain the same number of phosphorus atoms, this variation is not necessarily dependent on or related to the differences in the combining power of the element.

Determinations of the refractive index of phosphorous oxide for the red lithium line, the sodium D line, the green thallium line and the three brightest hydrogen lines corresponding to C, F and G have led to the following general expression for the refraction of liquid phosphorous oxide at 27·4° : $\mu = 1{\cdot}5171 + \frac{817{,}670}{\lambda^2} - \frac{316{,}590{,}000{,}000}{\lambda^4}$.

The calculated value of μ for the line A (wave-length 7604) is 1·5311 : for a ray of infinite wave-length it is the first term of the above expression, viz., 1·5171. As the rel. den. of liquid phosphorous oxide at 27·4 is 1·9300, the refraction equivalent of phosphorous oxide for A is $\frac{220 \times 0{\cdot}5311}{1{\cdot}93} = 60{\cdot}5$; for a ray of infinite wave-length it is 58·9.

The bearing of this observation on the refraction equivalent of phosphorus is then discussed.

Contrary to the usual statement of the text books, cold water has very little action on phosphorous oxide : many days elapse before even a small quantity is dissolved ; it then forms phosphorous acid, H_3PO_3. Hot water acts upon P_4O_6 with explosive violence, forming the red suboxide, phosphoric acid and spontaneously inflammable phosphoretted hydrogen.

Caustic alkalis act similarly. On adding ethyl alcohol to the oxide it at once ignites, but with care the two compounds may be caused to interact to form *diethyl phosphite* or *diethyl phosphorous acid* in accordance with the equation $P_4O_6 + 8C_2H_6O = 4P\begin{cases} OC_2H_5 \\ OC_2H_5 \\ OH \end{cases} + 2H_2O$.

This substance, which will be described more fully in a subsequent paper by one of the authors and Mr. Parker North, is a liquid of intensely disagreable smell, of rel. den. 1·0749 at $\frac{15{\cdot}5}{4}$ and boiling at 184—185°. Ether, carbon bisulphide and benzene dissolve phosphorous oxide unchanged.

Phosphorous oxide spontaneously oxidises to phosphorus pentoxide on exposure to air or to oxygen, and the process of oxidation is attended under diminished pressure by a faint luminous glow. No ozone is formed as the oxidation proceeds. On gently warming the

oxide in oxygen, the glow gradually increases in intensity until it passes into flame. In warm oxygen the melted oxide at once ignites and burns with great brilliancy. Care, therefore, is necessary in distilling large quantities of phosphorous oxide to avoid the free access of air; otherwise dangerous explosions may occur.

In contact with ozone phosphorous oxide glows at the ordinary temperature and pressure.

A small quantity of the oxide thrown into a jar of chlorine at once inflames, but on leading a slow current of the gas over the cooled oxide it is gradually converted into phosphorus oxychloride and the metaphosphoryl chloride of Gustavson: $P_4O_6 + 4Cl_2 = 2POCl_3 + 2PO_2Cl$.

Phosphorous oxide has a well marked physiological effect, and it is not improbable that the action hitherto attributed to phosphorus, especially as regards its influence on the glycogenic functions of the liver and on tissue change, may be really due to this substance. It is well known that persons employed in the manufacture of lucifer-matches are occasionally attacked by caries of the lower jaw; this is not due to the action of the phosphorus after absorption into the circulation, but to the direct effect of the fumes upon the bone itself: for it has been found that when a bone of an animal fed by phosphorus was exposed no carious change took place; but if one were exposed to the fumes caries was produced, and amongst lucifer-match makers it has been noticed that only those who have carious teeth suffer from necrosis of the jaw (T. Lauder Brunton, *Pharmacology, &c.*, 771). The fumes from phosphorus consist largely of phosphorous oxide; by drawing air over phosphorus without allowing it to ignite and passing the fumes through a narrow strongly cooled tube a deposit is obtained which melts with the warmth of the hand and gives the reactions for phosphorous oxide. Moreover, the smell of the product is identical with that of pure phosphorous oxide, and it is also identical with the peculiar smell noticed in a lucifer-match manufactory during the making and handling of the "composition" with which the splints are "tipped" and which hangs about the benches where the "boxers" are at work. It is highly probable, as Schönbein long ago surmised, that phosphorus vapour as such is odourless, and that the smell which phosphorus ordinarily possesses is a mixture of that of ozone and of phosphorous oxide.

The authors are continuing the study of this compound, and have already investigated the action upon it of ammonia, sulphur, sulphuric acid, the chlorides of phosphorus &c.; they are also engaged in experiments on its behaviour with a number of organic substances, and they promise a further communication on an early date.

29. "The action of chlorine on water in the light, and on the action of light on certain chlorine acids." By Professor A. Pedler.

After referring to the somewhat discrepant statements on record regarding the action of chlorine on water in the light, the author describes a long series of experiments made in Calcutta, where the intensity of light is such that a strong solution of chlorine in water, when exposed to the full blaze of the sun during the hot season, is actually seen to effervesce very decidedly. The results show that interaction takes place only under certain conditions, and that more than one change is possible.

In a first series of experiments, known volumes of chlorine and water enclosed in tubes were exposed to light, and at the conclusion of the exposure the tubes were opened under water: the contraction having been measured, the residual chlorine and subsequently the oxygen which had been produced were estimated. Using 83·5 c.c. chlorine and 4 c.c. water, quantities in the ratio $Cl_2 : 64H_2O$, practically no action was found to have taken place after exposure during a month to strong diffused daylight, and during a second month to the direct action of tropical sunlight; but, the ratio being $Cl_2 : 88H_2O$, about 29 per cent. of the chlorine was found to have been active, 6·5 c.c. of oxygen being liberated. Supposing action to have taken place according to the equation $2H_2O + Cl_2 = O_2 + 4HCl$, 7 c.c. of oxygen should have been obtained, an indication that a very small portion of the chlorine had undergone oxidation. The general result of a number of experiments of this kind was that, even in very strong tropical sunlight, water and chlorine interact to but a very slight extent when there are about 100 times as many molecules of water present as of chlorine; when the proportion is about $150H_2O : Cl_2$, action takes place to the extent of perhaps nearly 50 per cent. of the possible amount; and, when more than $400H_2O : Cl_2$, interaction takes place much more rapidly, but even then only to about four-fifths of the theoretically possible extent. As the proportion of water is increased, the amount of chlorine which is oxidised becomes somewhat larger.

Chlorine water saturated at 30—32°, the average working temperature in a Calcutta laboratory, contains chlorine in about the ratio $708H_2O : Cl_2$. Experiment shows that, when exposed to direct tropical sunlight, such water undergoes decomposition practically entirely in the sense of the equation $2H_2O + 2Cl_2 = O_2 + 4HCl$, an exceedingly small amount of chloric acid being formed. On exposing it to strong diffused daylight inside an open south verandah, either hypochlorous or chloric acid, or both, were formed in somewhat variable amount, the proportion of oxygen being much below that obtained in the

previous experiments in bright sunlight. On exposing the chlorine water to very moderate diffused light opposite the window in a room having a north light, very little, if any, oxygen was liberated, but the chlorine became oxidised to hypochlorous and chloric acids. In no case could chlorous acid or hydrogen peroxide be detected.

On exposing dilute solutions of hypochlorous acid to light, it was found that both oxygen and chloric acid were produced, the proportion of oxygen being larger the greater the intensity of the light. Solutions of chloric acid underwent little or no change.

The author concludes that in its first stages, at all events, the action of chlorine on water is quite similar to that which it exercises on dilute cold solutions of sodium and potassium hydroxides; and that in the subsequent stage it is very similar to that effected in the case of more concentrated and hot solutions of the two hydroxides.

30. "Note on the explosion of hydrogen sulphide and of carbon bisulphide with air and oxygen." By Professor A. Pedler.

The author finds that when a mixture of hydrogen sulphide, air and oxygen is exploded, a normal result is obtained, sulphur dioxide and water being formed. But when carbon bisulphide vapour is similarly treated, a not inconsiderable proportion of the nitrogen of the air becomes oxidised; and after the explosion contraction continues to take place, owing to the formation of sulphuric compounds (chamber crystal, &c.) under the combined influence of the moisture present and the oxide of nitrogen. The results of a large number of experiments are described, showing the effect of various proportions of oxygen and air.

31. "The action of light on phosphorus, and on some of the properties of 'amorphous' phosphorus." By Professor A. Pedler.

As part of an extensive series of experiments on the action of strong light on substances, the author has studied its effect on phosphorus, and has thereby been led also to examine and compare the several forms of allotropic phosphorus, viz., that produced by the action of light only, that produced at moderate temperatures, the commercial form, and also rhombohedral or metallic phosphorus prepared by dissolving phosphorus in lead at high temperatures.

The conclusion is arrived at that the term "amorphous phosphorus" is a distinct misnomer, and that, so far from commercial "amorphous" phosphorus constituting a separate allotropic modification of the element, it is in reality the same substance as the form called rhombohedral or metallic phosphorus, the very slight differences in cha-

racter noticed between the substances in question being explained by the difference in the state of division and the slight variations conditioned by their mode of formation. Whether the term amorphous phosphorus can be truly applied to the forms made by the action of light is open to grave doubt; even in this case there appears to be distinct evidence of crystalline form, although, in some instances, a form which appeared to be amorphous was obtained. It is suggested that it would be better to altogether discard the use of the term *amorphous phosphorus*.

The author finds that when phosphorus is exposed to light in contact with liquids containing oxygen, such as alcohol, it tends to enter into action with them. He arrives at the conclusion that neither *in vacuo* nor at ordinary pressures is there any change whatever of red into ordinary phosphorus at 260° as ordinarily stated; and that, practically, no change occurs up to temperatures of nearly 358°, above which, *in vacuo*, change takes place, but exceedingly slowly, even up to 445°. He also describes experiments which tend to show that red phosphorus is not permanent in air, as commonly supposed.

32. "The action of phosphoric anhydride on fatty acids." By F. S. Kipping, Ph.D., D.Sc.

In a previous preliminary note published in these Proceedings, the author has described the formation of the ketone stearone by the action of phosphoric anhydride on stearic acid; he now gives a detailed account of his experiments with this acid, and also describes the application of the same method to the preparation of dihexyl ketone, $(C_6H_{13})_2CO$, from heptylic acid. Two experiments gave 33 and 25 per cent. respectively of the theoretical amount of dihexyl ketone; the yield of stearone being 40—42 per cent. of the theoretical.

Dihexyl ketone is found to have the properties already described by Uslar and Seekamp (*Annalen*, **106**, 179). Its hydroxime and hydrazone were both obtained as yellow oils. Dihexyl carbinol was prepared by adding a large excess of sodium to an ethereal solution of the ketone placed in a flask together with moderately concentrated soda solution; it crystallises from dilute alcohol in plates melting at 41—42°.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Companion to the latest edition of the British Pharmacopœia, by Peter Squire. Fifteenth edition, revised by P. W. Squire and A. H. Squire. London 1890. From P. W. Squire, Esq.

II. *By Purchase.*

Les Engrais, par A. Müntz et A. C. Girard. Deux tomes. Tome I, Alimentation des plantes; fumiers; engrais des villes; engrais végétaux. Tome II, Engrais azotés: engrais phosphatés. Paris 1889.

A Text-Book of Assaying for the use of those connected with Mines. By C. Beringer and J. J. Beringer. London 1889.

The Micro-organisms of Fermentation practically considered. By A. Jörgensen. Edited from the German by G. H. Morris. London 1889.

SPECIAL MEETING, MAY 8th.

Fellows who desire to exhibit objects at the Special Meeting in May are requested to communicate *forthwith* with the Secretaries, in order to give time for the preparation of a descriptive list of the exhibits.

At the next meeting, on May 1st, the following paper will be read:—

"The conditions under which hydrogen peroxide is formed from ether." By Prof. Dunstan and T. S. Dymond.

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Issued 9/5/1890.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 83. Session 1890–91.

May 1st, 1890. Dr. W. J. Russell, F.R.S., President, in the Chair.

Messrs. Joseph Barker and Thomas Flower Ellis were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Wallis Jenkins, 9, Arnold Street, Anlaby Road, Hull; John McKillop, Pulau Brani, Singapore; John Brooks Thornley, Ivanhoe Terrace, Ashby-de-la-Zouch.

The following papers were read:—

33. "An investigation of the conditions under which hydrogen peroxide is formed from ether." By Professor Wyndham R. Dunstan and T. S. Dymond.

The authors have investigated the conditions under which hydrogen peroxide is formed from ether. The ether used by them was purified by the usual method, and also by repeated agitation with dilute aqueous chromic acid.

Contrary to the usual statement, the authors find that pure ether, either wet or dry, does not form hydrogen peroxide when exposed to light (daylight or electric light).

Ether prepared from methylated spirit yields hydrogen peroxide when kept for some time, but not if it has been previously purified by means of dilute chromic acid.

Neither water nor dilute sulphuric acid forms hydrogen peroxide when exposed to light in contact with air.

Hydrogen peroxide is formed when ozone acts on ether in the presence of water.

Hydrogen peroxide is produced when certain conditions are maintained during the slow combustion of ether in contact with water. At a low red heat the ether and oxygen appear to interact in a manner similar to that in which ozone and ether interact.

Discussion.

Dr. Richardson said that everything depended on the nature of the glass of the bottles in which the liquids were exposed, and the quality of the light. The authors had spoken of Winchester bottles. Of what kind of glass were the bottles which had been used made? With regard to the method which he had adopted in purifying his ether, so-called pure ether was shaken with water, and then repeatedly distilled from sodium until at last this was unaffected. His more recent experiments led him still to believe that peroxide was formed from water and oxygen on exposure to light.

Professor Ramsay, speaking of the purification of ether, referred to the investigation of the thermal properties of ether by Professor Young and himself. Regnault states that ether, after standing, no longer has a constant boiling point, and they had found that such ether acts on mercury but that after agitation with mercury and distilling it does so no longer. Professor Young and he had prepared ether from alcohol and sulphuric acid, and after washing it with potash and with sulphuric acid, had found it necessary to agitate it about fifty times with water before the iodoform test ceased to afford evidence of the presence of alcohol. Proof that such ether was pure was afforded by the agreement of the determinations of its vapour pressure made by the static and dynamic methods; four specimens were found to give identical results. Some of the authors' specimens may have contained alcohol. He then referred to the experiments which he had made showing that hydrogen peroxide is produced on evaporating water (these Proceedings, 1886, 225).

Mr. Wood asked if any observations had been made of the temperature during exposure; the amount of ether vapour would vary greatly with the temperature. In India he had frequently noticed that ether liberated iodine, but its behaviour in this respect was extremely capricious; he could scarcely think that the very different behaviour of several bottles of one consignment was due to impurity.

Professor Dunstan, in reply to Dr. Richardson, stated that colourless Winchester bottles were employed. The specimen of impure ether which yielded hydrogen peroxide scarcely affected potassium

iodide before exposure; another similar specimen had no action on the iodide. He had not been able to confirm Dr. Richardson's statement that hydrogen peroxide is formed when acidified water is exposed to light together with oxygen. In reply to Dr. Ramsay, he stated that the method used to purify the ether must have resulted in the entire removal of alcohol. The experiments now recorded proved that under certain well-defined conditions hydrogen peroxide was not formed from pure ether. It was for those who, like Dr. Richardson and Professor Ramsay, maintained that it is produced under similar circumstances to point out what the necessary condition is. This had not yet been done, and in fact so far apparently no one had suspected that the result might be due to an impurity. He had not been able to detect any hydrogen peroxide in water which had been heated in the manner described by Professor Ramsay in contact with air, although the experiment had been tried many times. With reference to Mr. Wood's remarks, the conditions under which the ether had been exposed were fully described in the paper; the temperature ranged between 15—25°. In London it was not possible to obtain "intense sunlight," but it seemed well established that the electric light is highly active in influencing chemical change. There was evidence that ether prepared from ordinary alcohol sometimes, but not invariably, contains the impurity from which hydrogen peroxide is formed; in any case this impurity would be removed by treatment with chromic acid. As was stated in the paper, the formation of an oxidising substance by the imperfect combustion of ether, to which Mr. Wood had referred, had been observed long ago: in fact Faraday had shown the experiment in his lectures on ozone. It is established by the present results that pure ether yields hydrogen peroxide when it is imperfectly oxidised in contact with cold water.

In reply to the President, he said that, although the period of exposure was the same in the case of the experiments with purified ether, they were made at a later date.

34. "*p*-Desylphenol." By Francis R. Japp, F.R.S., and G. H. Wadsworth, Associate of the Normal School of Science.

The authors find that by the action of cold concentrated sulphuric acid on a mixture of benzoïn and phenol *p*-desylphenol-monosulphonic acid is formed: $C_{14}H_{12}O_2 + C_6H_5{\cdot}OH + H_2SO_4 = C_{20}H_{15}O_2(SO_3H) + 2H_2O$; and that on heating this with concentrated chlorhydric acid at 150° it is hydrolysed, yielding *p*-desylphenol, $C_6H_5{\cdot}CO{\cdot}CH(C_6H_5){\cdot}C_6H_4{\cdot}OH$. This phenol crystallises from light petroleum in small, colourless laminæ melting at 133°; from dilute alcohol in large, thin laminæ; and from benzene in warty aggrega-

tions with 1 mol. of benzene of crystallisation. It dissolves in caustic alkalis, and is reprecipitated by carbon dioxide.

When heated with acetic anhydride it yields a monacetyl-derivative, $C_{20}H_{15}(C_2H_3O)O_2$, which forms aggregations of slender, white needles melting at 106—107°.

By acting on the sodium salt with methyl iodide, *p*-desylanisoïl, $C_6H_5{\cdot}CO{\cdot}CH(C_6H_5){\cdot}C_6H_4{\cdot}OCH_3$, is obtained. It melts at 90—92°, and is insoluble in caustic alkalis.

On fusion with caustic potash at 200°, *p*-desylphenol is resolved into benzoic acid and *p*-benzylphenol. If the temperature be carried higher the *p*-benzylphenol is oxidised to *p*-hydroxybenzoic acid. On reduction with sodium and boiling amyl alcohol, it is converted into the compound $C_6H_5{\cdot}CH(OH){\cdot}CH(C_6H_5){\cdot}C_6H_4{\cdot}OH$, which crystallises from benzene in tufts of slender needles melting at 161—162°, and yields a diacetyl-derivative melting at 156—157°. Iodhydric acid and amorphous phosphorus at 130°, on the other hand, reduce *p*-desylphenol to dibenzyl and phenol, a carbon linkage being severed in the interaction.

It yielded no hydroxime or phenylhydrazone, although it was subjected to the action of hydroxylamine and of phenylhydrazine under a variety of the most favourable conditions. This negative evidence might be regarded as an indication that the compound does not contain a carbonyl-group: but, apart from the fact that such evidence is not conclusive, the alternative formula in which, for the sake of getting over the difficulty, a union of one oxygen-atom to two directly linked carbon-atoms might be assumed, has so little antecedent probability that the authors hesitate to put it forward, and in the meantime continue to regard the compound as *p*-desylphenol, a constitution with which all its other interactions are in harmony.

Attempts to prepare similar condensation-products of benzoïn with other phenols led to no result.

35. "On Benedikt's Acetyl values." By J. Lewkowitsch, Ph.D.

In his paper on a new method of examining fats (*Zeitschrift für die chemische Industrie*, 1887, p. 149), Benedikt proposes a method which is based on the principle that only hydroxylated fatty acids take up the radicle of acetic acid when heated with acetic anhydride, and he asserts that those fatty acids which do not contain the hydroxyl-group remain unaltered; so that the quantities of potash required for neutralising fatty acids before and after treatment with acetic anhydride will be either identical or nearly so, any difference being due to the errors of the method of determination.

While examining a somewhat abnormal sample of tallow, the

author was led to doubt the accuracy of this statement, and the following results of experiments which he has made serve to confirm his doubts.

The fatty acids prepared from a sample of fresh town tallow required for neutralisation 19·717 per cent. of potash, or, in other words, their "acid value" was equal to 19·717, corresponding to the molecular weight 284·5. 50 grams of these acids was acetylated with 40 grams of acetic anhydride in the manner indicated by Benedikt, and both the acid value and the "saponification" value of the acetylated product were then determined. The values found were 160·5 and 217·5 respectively, corresponding to an acetyl value of 217·5 — 160·5 = 57. A second test gave 216·3 — 159·9 = 56·4.

In the same way the fatty acids of samples of South American tallow and of North American tallow gave the acetyl values 77·8 and 23·93. According to Benedikt the acetyl values ought to have been *nil* or nearly so.

As tallow is considered to consist essentially of a mixture of the glycerides of stearic, palmitic and oleic acids, it was thought possible that it was the oleic acid which had fixed the acetic acid radicle. A sample of oleic acid obtained from Kahlbaum as pure was therefore examined; it contained, however, some solid acids, which settled out when the acid was kept for some time in a stoppered bottle. To determine the impurities, the acid value and iodine absorption were ascertained: the acid value found was 183, and the iodine absorption 90·14; the theoretical values for oleic acid are 198 and 90·07. Although containing a certain amount of higher homologues, the acid was considered sufficiently pure for the desired purpose: 50 grams of it when acetylated gave an acid value = 116·50 and a saponification value = 242·05; consequently an acetyl value = 125·55. If the fixing of the "acetyl," however unlikely it might appear, were due to the CH=CH-group in the molecule of the oleïc acid, the acetylated acids ought to have lost the capacity of taking up iodine. However, the iodine value of the acetylated acids was found to be 87·11, proving clearly that acetyl was not taken up by the CH=CH-group. Therefore, the acetic anhydride must have acted in some other way on the oleic acid, and if so it was not unlikely that palmitic or stearic acid might be acted on in the same way: experiment fully bore out the correctness of this assumption.

50 grams palmitic acid, the comparative purity of which was proved by an acid value of 213·4 (instead of the theoretical value 219·1), was acetylated and gave an acid value = 143·53 and a saponification value = 226·13; consequently an acetyl value = 82·6.

50 grams stearic acid—showing an acid value of 203 instead of the theoretical one of 197·5—gave, after being acetylated, an acid value

= 138·89 and a saponification value = 221·18; consequently an acetyl value = 82·29.

The author refrains from venturing upon an explanation of these results, merely wishing to point out at present that they contradict Benedikt's assumptions.

RESEARCH FUND.

Fellows desiring grants are requested to forward their applications to the Secretaries in order that they may be considered at the next meeting, in June.

At the next meeting, on May 15th, there will be a ballot for the following candidates :—

1. Appleyard, James Robert, University College, Dundee.
2. Blake, William Henry, 31, Norfolk Street, Sunderland.
3. Colwell, James Kear, 2, Lloyd Street, Lloyd Square, W.C.
4. Copeman, S. Sydney Monckton, M.A., M.B. Cantab., 134, York Road, S.E.
5. Caird, George, 20, Springfield, Dundee.
6. Fairgrieve, Andrew, Sydney, New South Wales.
7. Findlay, G. H., Hawthorn Cottage, Francis Road, Edgbaston, Birmingham.
8. German, George, Junr., Huntingdon House, Ashby-de-la-Zouch.
9. Jones, John Archyll, 3, Jedburgh Street, Middlesbrough.
10. Kirk, Oliver, Science Schools, South Kensington, S.W.
11. Oddy, Robert Walter, Waterhouse, Toad Lane, Rochdale.
12. Tate, William, 115, Rylston Road, Fulham, S.W.

The following papers will be read :—

"Diethylphosphorous acid." By Prof. Thorpe, F.R.S, and Mr. Barker North.

"Researches on naphthalene-derivatives. The ten isomeric dichloronaphthalenes. The action of chlorine on naphthalene and its derivatives." By Dr. Armstrong and Mr. Wynne.

"A third naphthaquinone." By Prof. Meldola, F.R.S., and Mr. F. Hughes.

HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY, ST. MARTIN'S LANE.

Issued 31/5/1890.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 84. Session 1890–91.

May 15th, 1890. Dr. W. J. Russell, F.R.S., President, in the Chair.

Mr. James Hamilton was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Charles F. Branson, Kenley Lodge, Macaulay Road, Clapham Common; John Huchinson Edward, 117, Stockport Road, Manchester; Arthur R. Haslam, Ph.D., 64, Rathgar Road, Dublin; John Robert Johnson, 16, Oxford Street, Liverpool; Patrick Kelly, 43, Lennox Street, Dublin; Thomas Parker, M.I.C.E., Wolverhampton; Richard James Redding, Royal Laboratory, Woolwich Arsenal; Frederick Smith, Johannesberg, Transvaal, South Africa.

The following were elected Fellows of the Society:—

James Robert Appleyard; William Henry Blake; James Kear Colwell; S. Sydney Monckton Copeman, M.A., M.B.; Andrew Fairgrieve; G. H. Findlay; John Archyll Jones; Oliver Kirk; Robert Walter Oddy; William Tate.

The following papers were read:—

36. "Diethylphosphorous acid" By T. E. Thorpe, F.R.S., and Barker North, Associate of the Normal School of Science.

The authors describe the mode of preparing this compound and its properties. It is obtained by adding alcohol, drop by drop, to phosphorous oxide contained in a vessel surrounded with ice and salt. It is a colourless, mobile liquid, possessing a peculiar penetrating

alliaceous smell. Its vapour is poisonous, and even small quantities produce headache and nausea. It boils at 184—185°, and has the relative density 1·0749 at $\frac{15{\cdot}5^\circ}{4}$. It interacts with water forming alcohol and phosphorous acid, and is converted by bromine into ethyl bromide and metaphosphoric acid.

37. "The homonucleal trichloronaphthalenes." By Henry E. Armstrong and W. P. Wynne.

1 : 2 : 3-*Trichloronaphthalene.*—The compound prepared by Faust and Saame from α-chloronaphthalene tetrachloride has been shown by Widman to be this modification, the proof being that it affords nitrotrichlorophthalic acid on oxidation with nitric acid; the authors have obtained it from a novel source—by the action of phosphorus pentachloride on Zincke and Kegel's αβ-dichloro-β-naphthol (*Berichte*, 1888, 3385). This naphthol-derivative is found to crystallise in aggregates, such as Zincke and Kegel describe, of long, prismatic needles springing from a common centre—m. p. 76—77°; also (*a*) in fairly large aggregates composed of characteristic short, stumpy prisms—m. p. 76—77°; and (*b*) in very long, slender, flat, transparent needles melting at 66°, and on refusion at 74°. In no case was a higher melting point than 77° observed. Zincke and Kegel, however, give 81° as the melting point of the substance; and it is noteworthy, therefore, that the authors find the melting point of trichloroketonaphthalene to be 92—93°, instead of 96°, and that one of them, in conjunction with Mr. Rossiter, has found that the various chloro-derivatives of β-naphthol described by Zincke and Kegel uniformly melt at temperatures about 4° lower than stated by these chemists; it may also be mentioned that a similar discrepancy is to be noted in the case of a recent paper of Clausius (*Berichte*, 1890, 517), who specially calls attention to the fact that he finds the melting point of 2 : 2′-dihydroxynaphthalene to be 4° *higher* than previously observed.

αβ-Dichloro-β-naphthol exchanges its hydroxyl for chlorine when distilled with the theoretical quantity of phosphorus pentachloride at 240—250°. The resulting trichloronaphthalene crystallises from alcohol, in which it is sparingly soluble in the cold, either in long, very slender needles or in radiate aggregates of flat needles; it melts at 81°. It is but little acted on when heated at 100° with H_2SO_4, but is readily sulphonated when digested with four times its weight of acid containing 10 per cent. SO_3 for an hour at 100°. The *barium* salt of the acid, $(C_{10}H_4Cl_3SO_3)_2Ba + 3\frac{1}{2}H_2O$, crystallises in small, spherical aggregates, and is sparingly soluble in water; the *potassium* salt, $C_{10}H_4Cl_3SO_3K$, is very soluble in water, but sparingly soluble in

alcohol, from which it crystallises in minute, anhydrous needles. The *chloride*, $C_{10}H_4Cl_3{\cdot}SO_2Cl$, crystallises from benzene, in which it is very soluble, in small, prismatic needles; from petroleum spirit, in which it is sparingly soluble, in small, flat, slender needles; and from acetic acid in white aggregates of very small needles; it melts at 182°. The *amide* could not be obtained crystalline: it melts at 296°. The chloride was hydrolysed by prolonged heating with concentrated muriatic acid at 260°: the regenerated trichloronaphthalene crystallised from alcohol in long, slender needles melting at 81°.

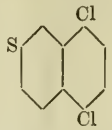
1 : 2 : 4-*Trichloronaphthalene.*—This modification was first prepared by Cleve, who most accurately described its properties (*Berichte*, 1888, 893), from dichloralphanaphthol; the authors prefer to prepare it from dichloralphanaphthylamine. It melts at 92°. When sulphonated, either by means of the theoretical quantity of SO_3HCl, or by heating with twice its weight of H_2SO_4 at 100° for one hour, it yields an acid which when dissolved in water forms a viscid solution —in this respect resembling the acid obtained by sulphonating 1 : 4-dichloronaphthalene. The *barium* salt $(C_{10}H_4Cl_3SO_3)_2Ba + 3H_2O$ is very sparingly soluble in water, and crystallises in fluffy masses of very small, slender needles; the *potassium* salt $C_{10}H_4Cl_3SO_3K$ is extremely soluble in water, but sparingly soluble in alcohol, from which it crystallises in anhydrous, short, slender needles. The *chloride* $C_{10}H_4Cl_3SO_2Cl$ crystallises from benzene in tufts of long, slender needles; from petroleum spirit, in which it is sparingly soluble, in long, slender needles; and from acetic acid in slender, flat needles; it melts at 157—158°. The *amide* crystallises from alcohol in tufts of short, slender needles, and melts at 235°. The chloride was hydrolysed with considerable difficulty, requiring prolonged heating at 260—265° with concentrated muriatic acid: the resulting trichloronaphthalene crystallised from alcohol in tufts of slender, flat needles melting at 92°.

38. "The ten isomeric dichloronaphthalenes and the sulphonic acids and trichloronaphthalenes derived therefrom." By Henry E. Armstrong and W. P. Wynne.

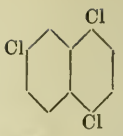
Whereas, theoretically, only *ten* dichloronaphthalenes are possible, *twelve* have actually been described. Nine of these are already proved to be definite substances, and their constitution may be regarded as well established (*cf.* these Proceedings, 1888, 104; 1889, 34, 48); these nine include the three possible $\alpha\alpha$-, the four possible $\alpha\beta$- and the two possible hetero-$\beta\beta$-compounds. Of the remaining three, one—the so-called α-dichloronaphthalene (m. p. 38°)—has been shown by the authors to be non-existent, and to consist of the

αα-Dichloronaphthalenes.

M. p. = 67·5°.



SO_2Cl, m. p. = 132°.
SO_2NH_2, m. p. = 244°.

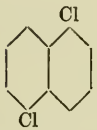


M. p. = 66°.

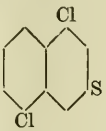
M. p. = 82°.

SO_2Cl, m. p. = 114°.
SO_2NH_2, m. p. = 228°.

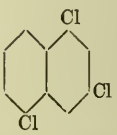
M. p. = 131°.



M. p. = 106·5°.



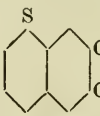
SO_2Cl, m. p. = 139·5°.
SO_2NH_2, m. p. = 204°.



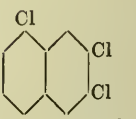
M. p. = 103°.

ββ-Dichloronaphthalenes.

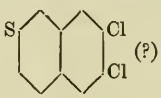
M. p. = 119·5°.



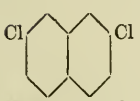
SO_2Cl, m. p. = 142°.
SO_2NH_2, m. p. = 268°.



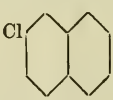
M. p. = 109·5°.



SO_2Cl, m. p. = 178°.

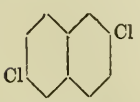


M. p. = 114°.

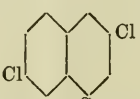


SO_2Cl, m. p. = 163·5°.
SO_2NH_2, m. p. = 218°.

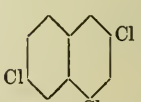
M. p. = 91°.



M. p. = 135°.

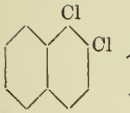


SO_2Cl, m. p. = 136°.
SO_2NH_2, m. p. = 269°.

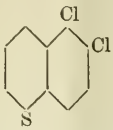


M. p. = 113°.

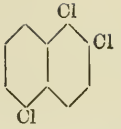
αβ-Dichloronaphthalenes.



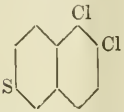
M. p. = 35°.



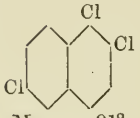
SO_2Cl, m. p. = 104°.
SO_2NH_2, m. p. = 217.°



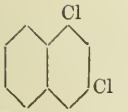
M. p. = 78·5°.



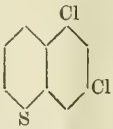
SO_2Cl, m. p. = 167·5°.
SO_2NH_2, m. p. = 190°.



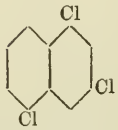
M. p. = 91°.



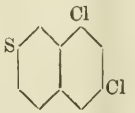
M. p. = 61°.



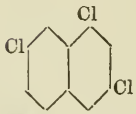
SO_2Cl, m. p. = 148·5°.
SO_2NH_2, m. p. = 272°.



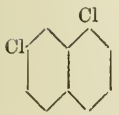
M. p. = 103°.



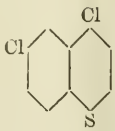
SO_2Cl, m. p. = 121°.
SO_2NH_2, m. p. = 228°.



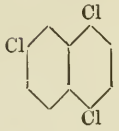
M. p. = 113°.



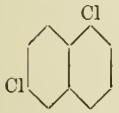
M. p. = 62·5—63·5°.



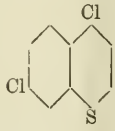
SO_2Cl, m. p. = 118°.
SO_2NH_2, m. p. = 226°.



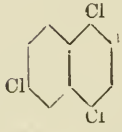
M. p. = 66°.



M. p. = 48°.



SO_2Cl, m. p. = 151°.
SO_2NH_2, m. p. = 216°.



M. p. = 66°.

1 : 3- (m. p. 61°) and 1 : 4- (m. p. 68°) modifications (these Proceedings, 1888, 106). A second is undoubtedly also non-existent, viz., the "κ-dichloronaphthalene" (m. p. 94°), which, according to Claus (*Ber.*, 1882, 314), is obtained by the action of phosphorus pentachloride on the α-naphtholsulphonic acid prepared by sulphonating α-naphthol dissolved in acetic acid. The several monosulphonic acids formed from α-naphthol, however, correspond to one or other of the nine recognised dichloronaphthalenes, and on this ground alone the production of the tenth, and—it is to be supposed—only possible, modification in such a manner appears impossible: even if the fact be left out of account that *homo*-ββ-dichloronaphthalene—the only modification required in addition to the nine above specified in order to complete the list—cannot be prepared from *alpha*-naphthol. α-Naphthol is converted, with exceptional facility, into the 1 : 2 : 4-disulphonic acid, and the corresponding trichloronaphthalene melts at 92°, which is very nearly the melting point of Claus's compound; the authors, therefore, have little doubt that the substance described by Claus as κ-dichloronaphthalene was in reality 1 : 2 : 4-trichloronaphthalene.

The only remaining modification to be considered is the ι-dichloronaphthalene (m. p. 120°), first prepared by Leeds and Everhard by heating naphthalene tetrachloride with silver oxide, and which was subsequently separated by Widman from the product of the action of alcoholic potash on the tetrachloride; until it was discovered that α-dichloronaphthalene was a mixture of the 1 : 3- and 1 : 4-compound, the authors were inclined to think that perhaps this modification was impure ε-dichloronaphthalene (*cf. B. A. Report*, 1888), but the necessity for this assumption occasioned by the existence of the α-compound having been removed, it appeared highly probable that the ι-compound was the homo-ββ-modification; and this proves to be the case, the authors having succeeded in obtaining a substance with all the properties ascribed by Leeds and Everhard and by Widman to ι-dichloronaphthalene by a novel method which places its constitution beyond all doubt, viz., by partially reducing 1 : 2 : 3-trichloronaphthalene.

The existence of a complete series of ten isomeric dichloronaphthalenes may, therefore, now be regarded as established. No fewer than eight of these have been discovered by Cleve and his pupils; all who study the subject must be led to admire the work of the Swedish chemists and to recognise the influence which it has exercised.

In order to characterise the various dichloronaphthalenes, and also to determine the manner in which constitution affects the course of chemical change in the case of naphthalene-derivatives, the authors

have sulphonated the ten modifications, and have converted the resulting sulpho-acids into trichloronaphthalenes. A brief account of the results is now given, details with reference to the composition of the salts, &c., being reserved for a full communication.

To avoid the possibility of the occurrence of secondary changes induced by the presence of water, chlorosulphonic acid was throughout employed as the sulphonating agent instead of sulphuric acid, and sulphonation was effected by adding slightly less than the theoretical quantity of this agent to a 10 per cent. solution of the dichloronaphthalene in dry carbon bisulphide; the carbon bisulphide was subsequently removed by distillation on a water-bath, the acid dissolved in water and the solution steam-distilled to free it from unattacked dichloronaphthalene and traces of carbon bisulphide, and finally filtered to remove the small proportion of insoluble, non-volatile compound (sulphochloride or sulphone) always formed.

αα-Dichloronaphthalenes.

(1.) 1 : 4-*Dichloronaphthalene.*—On sulphonation, this yields a practically uniform product, a very small proportion of an isomeric acid of undetermined constitution being simultaneously formed. The *chloride* of the acid, $C_{10}H_5Cl_2SO_2Cl$, crystallises from benzene, in aggregates of slender, prismatic needles melting at 132°; the *amide* is sparingly soluble in cold alcohol, crystallising in tufts of very slender, long needles melting at 244°. The corresponding *trichloronaphthalene* crystallises in tufts of slender needles, which, on standing, undergo conversion into opaque, white aggregates melting at 66° (*cf.* these Proceedings, 1890, 18). The sulphochloride undergoes hydrolysis when heated with concentrated muriatic acid at 260—265°; the pure dichloronaphthalene thus obtained crystallised from alcohol in long, narrow, slender ribbons melting at 67·5°.

(2.) 1 : 1′-*Dichloronaphthalene* was prepared by Atterberg's method (*Ber.*, 1876, 1732) from β-dinitronaphthalene. The sulphonation product consists of a single acid, the *chloride* of which crystallises from petroleum spirit in minute aggregates melting at 114°; the *amide* crystallises from alcohol in tufts of small, slender needles melting at 228°. The corresponding *trichloronaphthalene* crystallises from alcohol in very long, slender needles melting at 131°.

(3.) 1 : 4′-*Dichloronaphthalene* yields two acids on sulphonation; one of these is formed in small quantity only, and has not been completely examined. The chief product yields a *chloride* which crystallises from benzene in aggregates of long, flat, thin, narrow plates melting at 139·5°; the *amide* crystallises in small, prismatic aggregates melting at 204°. The corresponding *trichloronaphthalene*

crystallises from alcohol in long, slender needles melting at 103°. On hydrolysing the acid at 260—265° with concentrated muriatic acid, pure 1 : 4′-dichloronaphthalene was obtained, which crystallised from alcohol in short, flat, thin scales melting at 106·5°.

αβ-Dichloronaphthalenes.

(4.) 1 : 2-*Dichloronaphthalene* is found to yield a mixture of an *α*- and a *β*-sulphonic acid, the former constituting about two-thirds of the product.

The chlorides of the two acids require to be mechanically separated after crystallisation from benzene.

α-Acid.—The chloride crystallises from benzene, in which it is very soluble, in large, prismatic forms melting at 104°; the *amide* crystallises from alcohol in tufts of small, slender needles and melts at 217°. The corresponding *trichloronaphthalene* crystallises from alcohol in short, flat needles melting at 78·5°. On hydrolysis with concentrated muriatic acid at 230°, the chloride gave pure 1 : 2-dichloronaphthalene melting at 35°.

β-Acid.—The *chloride* of the *β*-acid is less soluble in benzene, and crystallises in aggregates of small prisms melting at 167°; the *amide* crystallises from dilute alcohol in short, slender, white needles melting at 190°. The corresponding *trichloronaphthalene* crystallises from alcohol in slender needles and melts at 91°. On hydrolysis with concentrated muriatic acid at 260—265°, the *β*-chloride gave pure 1 : 2-dichloronaphthalene melting at 35°.

(5.) 1 : 3-*Dichloronaphthalene.*—On sulphonation this yields a mixture of an *α*- and a *β*-acid, the former constituting about four fifths of the product.

The *chloride* of the *α*-acid crystallises from benzene in well-defined prisms melting at 148·5°, and crystallographically identical with those of the chloride of Widman's dichloronaphthalene-*α*-sulphonic acid; the *amide* is sparingly soluble in alcohol and crystallises in flocks of microscopic needles melting at 272°. The corresponding *trichloronaphthalene* crystallises from alcohol in long, slender, flat needles melting at 103°. On hydrolysis with concentrated muriatic acid at 230°, the *α*-chloride gave pure 1 : 3-dichloronaphthalene, which crystallised in long, slender ribbons melting at 61°.

The *β*-acid, although the minor product of sulphonation, constitutes the sole product when the sulphonation product is heated in a dry atmosphere at 160° for 18 hours. Its *chloride* is very soluble in benzene and crystallises best from a mixture of benzene and petroleum spirit in long, narrow, four-sided prisms melting at 121°; the *amide* crystallises from alcohol in tufts of short, very slender needles, and

melts at 228°. The corresponding *trichloronaphthalene* is sparingly soluble in hot alcohol and crystallises in short, slender needles melting at 113°. On hydrolysis with concentrated muriatic acid at 260—265°, the β-chloride gave pure 1 : 3-dichloronaphthalene melting at 61°.

(6.) 1 : 2′-*Dichloronaphthalene* yields an almost uniform product on sulphonation, the proportion of isomeric acid formed being very small. The *chloride* of the chief product crystallises from benzene in transparent, slender, flat needles which rapidly became opaque on exposure to the air, and then melt at 118°; the *amide* is sparingly soluble in alcohol and crystallises in narrow, slender ribbons melting at 226°. The corresponding *trichloronaphthalene* crystallises from alcohol in slender, flat needles which, on standing in the solvent, became opaque and melted at 66°. On hydrolysis with concentrated muriatic acid at 230°, the chloride gave pure 1 : 2′-dichloronaphthalene, which crystallised from alcohol in small, crystalline aggregates melting at 62·5°. The synthetical 1 : 2′-dichloronaphthalene, prepared by Erdmann's method, was found to melt slightly higher, viz., at 63—63·5°.

(7.) 1 : 3′-*Dichloronaphthalene* yields an uniform product on sulphonation. The *chloride* of the acid crystallises from benzene in magnificent prisms and melts at 151°; the *amide* crystallises from alcohol in long, slender needles melting at 216°. The corresponding trichloronaphthalene crystallises from alcohol in slender, flat needles which become opaque on standing in the solvent and melt at 66°. On hydrolysis with concentrated muriatic acid at 230°, the chloride gave pure 1 : 3′-dichloronaphthalene, which crystallised from alcohol in long, slender ribbons melting at 48°.

ββ-Dichloronaphthalenes.

(8.) 2 : 3-*Dichloronaphthalene*. To prepare this modification a solution of 1 : 2 : 3-trichloronaphthalene in alcohol heated at 60—70° is treated with one and a half times the theoretical quantity of 2 per cent. sodium amalgam during one hour; the ι-dichloronaphthalene is purified by fractional steam-distillation and fractional crystallisation from alcohol. It crystallises in the manner described by Leeds and Everhard and by Widman, in thin, lustrous scales, and melts at about 120°. On sulphonation it yields a product containing an α-acid and probably a β-acid, the former constituting the chief product. The *α-chloride* crystallises from benzene in lustrous, slender, narrow ribbons melting at 142°; the *amide* is sparingly soluble in alcohol and crystallises in aggregates of small, slender needles melting at 268°. The corresponding trichloronaphthalene crystallises from alcohol in long and very slender needles, and melts at 109·5°. On hydrolysis with con-

centrated muriatic acid at 230°, the α-chloride was found to yield pure 2 : 3-dichloronaphthalene, which crystallised from alcohol in the characteristic thin scales melting at 119·5°.

Isomeric Acid.—The salts of this acid have not yet been obtained in quantity sufficient for analysis. The *chloride* is very soluble in benzene and crystallises in opaque, hemispherical aggregates melting at 178°; on hydrolysis with concentrated muriatic acid at 260—265°, it gave 2 : 3-dichloronaphthalene melting at 119·5°. There can be little doubt that this acid has the constitution [$Cl_2 : SO_3H$ = 2 : 3 : 2′].

(9.) 2 : 2′-*Dichloronaphthalene* yields an almost uniform product on sulphonation, the proportion of isomeric acid formed being very small. The *chloride* of the chief product crystallises from benzene in well-formed, elongated prisms, and melts at 163·5°; the *amide* crystallises from dilute alcohol in tufts of long, slender needles, and melts at 218°. The corresponding *trichloronaphthalene* crystallises from alcohol in minute plates and melts at 90·5—91°. On hydrolysis with concentrated muriatic acid at 260—265°, the chloride gave pure 2 : 2′-dichloronaphthalene, which crystallised from alcohol in large, thin laminæ melting at 114°.

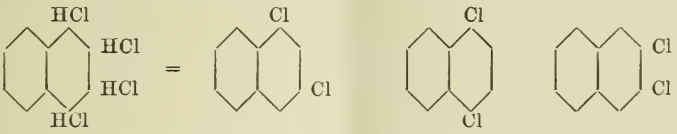
(10.) 2 : 3′-*Dichloronaphthalene* affords an almost uniform sulphonation product, the proportion of isomeric acid formed being small; the *chloride* of the chief product crystallises from benzene in radiate groups of long, slender, prismatic needles melting at 136°; the *amide* is sparingly soluble in alcohol and crystallises in small aggregates of prismatic needles melting at 269°. The corresponding *trichloronaphthalene* is sparingly soluble in alcohol and crystallises in small, slender needles melting at 113°. On hydrolysis with concentrated muriatic acid at 230°, the chloride gave pure 2 : 3′-dichloronaphthalene crystallising from alcohol in long narrow, ribbons melting at 135°.

It is noteworthy that the chlorides of the β-sulphonic acids require prolonged heating at a higher temperature than those of the α-acids to effect their hydrolysis; and that on distillation with phosphorus pentachloride they give a smaller yield of trichloronaphthalene.

In the table on pp. 78—79, the formulæ of the dichloronaphthalenes are given in the first column, those of the acids into which they are converted on sulphonation are given in the second, and the third comprises the trichloronaphthalenes obtained from the dichloronaphthalenesulphonic acids. The evidence on which the constitution of the tri-derivatives here given is based has been incidentally given in previous papers (*cf.* these Proceedings, 1889, 48; 1890, 11), and will be summarised in a forthcoming account of the trichloronaphthalenes.

39. "The chlorides of naphthalene and its derivatives, and the manner in which they are decomposed by alkalis." By Henry E. Armstrong and W. P. Wynne.

It being established that ι-dichloronaphthalene is the homo-$\beta\beta$-modification, it follows that naphthalene tetrachloride affords the three theoretically possible dichloronaphthalenes:

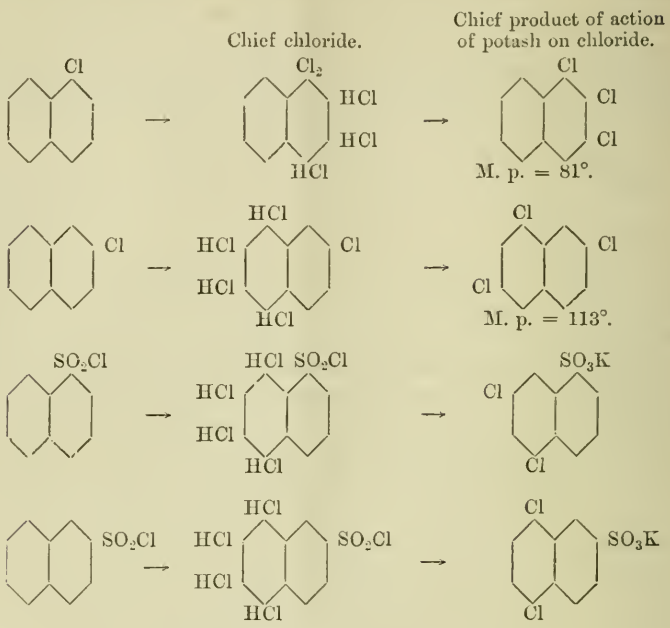


The 1 : 3-compound is produced in largest, the 2 : 3- in smallest, quantity.

Hitherto it has always been supposed that the dichloride which is the initial product of the interaction of naphthalene and chlorine decomposes only in one way, yielding α-chloronaphthalene; the authors find that β-chloronaphthalene is also produced. They have been led to this discovery by further study of the isomeric acid obtained in small quantity together with 1 : 4-chloronaphthalene-sulphonic acid from α-chloronaphthalene by Armstrong and Williamson (*cf.* these Proceedings, 1886, 233; *B. A. Report*, 1887): this acid proves to be identical with that obtained on sulphonating β-chloronaphthalene. In like manner, the secondary product obtained by Armstrong and Williamson from bromonaphthalene is derived from β-bromonaphthalene, which is present in ordinary bromonaphthalene even after considerable fractionation. The proportion of β-compound produced is but small in either case. This recognition of the presence of the β-compound in bromonaphthalene affords an explanation of Jolin's observation that the sulphonation product of bromonaphthalene contains an acid convertible into 2 : 3′-dibromonaphthalene.

The manner in which chlorine acts on derivatives of naphthalene, as well as that in which the resulting chlorides decompose, becomes of special interest now that Bamberger's researches have shown how very differently the α- and β-derivatives behave when hydrogenised; in the course of their experiments the authors have had occasion to collect a number of data bearing on this question, having re-examined the action of chlorine on the two chloronaphthalenes and the two monosulphochlorides. In each case, chiefly one tetrachloride is formed, and this decomposes chiefly in one way, the amount of subsidiary products in either case being relatively small; the exact nature of these subsidiary products has yet to be determined, and cannot be ascertained until considerable quantities of material have been operated on, and a more exact knowledge of some of the trichloro-

naphthalenes has been obtained. The results of their own and previous observations are summarised in the following table :—



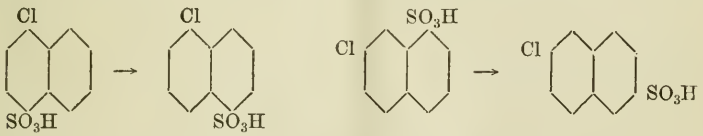
The influence of the substituent both as affecting the addition of chlorine and the elimination of hydrogen chloride is especially noteworthy. It will be seen that the sulphochlorides behave alike, but the two chloronaphthlenes dissimilarly towards chlorine, and that each compound decomposes in a manner peculiar to itself on treatment with alcoholic potash.

40. "Isomeric change in the naphthalene series. No. 6. The influence of position in determining the nature of the isomeric change in the case of the chloronaphthalenesulphonic acids." By Henry E. Armstrong and W. P. Wynne.

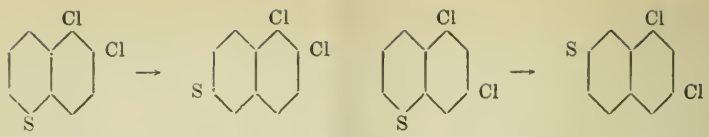
Arnell, in an "academic treatise" (*Bidrag till Kännedom om Naftalins Chlorsulfonsyror*; *Upsala*, 1889), in which a valuable summary is given of all that was known of the subject at the time of its publication, states that when α-chloronaphthalene is sulphonated by means of sulphuric acid it yields both the 1 : 4- and the 1 : 4′-derivative, the latter forming a large proportion of the product when the sulphonation is effected at an elevated temperature (160°) The formation of the 1 : 4′-acid when sulphonation was effected by means of

chlorosulphonic acid was overlooked by Armstrong and Williamson, but the experiments which they made on the effect of heating the initial product (these Proceedings, 1887, 145) led them to believe that the 1 : 4-acid was converted into the 1 : 4′-isomeride. Further study of the subject has shown that the 1 : 4′-acid is obtained in small quantity when a cold solution of α-chloronaphthalene is sulphonated by means of SO_3HCl, the product being heated only for a short time on the water-bath to remove the bisulphide; and that if the product be heated at about 150° during 5—6 hours, almost complete conversion into the 1 : 4′-acid is effected. It is therefore not improbable that the 1 : 4-acid is the only immediate product of sulphonation, and that the small quantity of the isomeride obtained at low temperatures is due to the occurrence of isomeric change at the moment of interaction.

The fact that the α-chloronaphthalene-derivative undergoes change into the more symmetrical *alpha*-isomeride, while 2 : 1′-β-chloronaphthalenesulphonic acid is converted in a similar manner into the more symmetrical *beta*-isomeride, appears to be noteworthy as indicating a tendency to a final state of symmetry, thus—



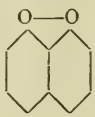
On reference to the tables at pp. 78—79, in which the constitution of the acids formed on sulphonating the ten dichloronaphthalenes is indicated, it will be observed that in some cases an α- and in some cases a β-sulphonic acid is formed, or a mixture of both. The authors are of opinion that the α-acid is always initially produced; in some cases this is so unstable that it spontaneously passes over into the β-isomeride and escapes observation, while in others it is partially preserved. They base this conclusion on the fact that in all cases hitherto studied in which both acids are formed it is possible to convert the α- into the β-acid by heating. Thus 1 : 2-dichloronaphthalene affords about two-thirds α- and one-third β-acid, but when the product is heated the latter is practically the sole product (*cf. B. A. Report*, 1889). In like manner the product of initial sulphonation from 1 : 3-dichloronaphthalene contains about one-fifth β-acid; but if this be heated at 160° during 18 hours complete conversion into the β-isomeride is effected. It is noteworthy that the position ultimately taken up by the SO_3H radicle appears to be determined by the *beta*-chlorine-atom, thus—



The β-sulphonic acids are probably the most "degraded" products, and from this point of view the further study of the behaviour of the 1 : 4′-α-chlorosulphonic acid and of the 1 : 1′ : 4-$\alpha\alpha$-dichlorosulphonic acids as well as that of the 2 : 1′- and 2 : 4′-$\alpha\beta$- and 2 : 3- and 2 : 3′-$\beta\beta$-dichlorosulphonic acids will be of special interest, in order to ascertain whether or no the determining factor is the tendency of the molecule to acquire a configuration which most nearly approaches symmetry.

41. "A third naphthaquinone." By R. Meldola, F.R.S., and F. Hughes.

In preparing monobromindone by the action of fuming nitric acid on dibrom-α-naphthol (*Proc.*, 1890, 57), a small quantity of a bye-product is obtained which remains undissolved in alcohol on treating the crude indone with this solvent; a sufficient quantity of this substance has been obtained by the authors to enable them to identify it as a new naphthaquinone. The pure substance forms slender, pale yellow needles, having no distinct melting point, but blackening about 220°. It is not reduced by sulphurous acid solution, but by treatment with zinc-dust and acetic acid it is converted into a dihydroxynaphthalene crystallising in whitish needles which become slate-coloured on exposure to the air and have no definite melting point but darken about 205°. The dihydroxynaphthalene has all the properties of a phenol, and is readily reconverted into the quinone by oxidation. Its diacetyl-derivative fuses at 226—227°. On oxidation with alkaline permanganate it affords 1 : 2 : 3-hydroxyphthalic acid, $C_6H_4(CH)(COOH)_2$ (m. p. 194—197°), and hence the authors conclude that the quinone is the unknown peri-derivative:—

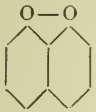


The formation of this quinone during the oxidation of dibrom-α-naphthol by nitric acid cannot at present be explained; the authors suggest that in the bromination of α-naphthol a minute quantity of *peri*-monobrom-α-naphthol is produced, and that this is converted into the quinone by the action of nitric acid.

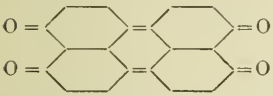
Experiments to test this explanation are in progress.

Discussion.

Dr. Armstrong said it appeared to him that, regarding the quinones as diketones, four true quinones could not be derived from naphthalene; the new compound described by the authors either had the constitution indicated by the formula which they had suggested,



, or it was a keto-compound of higher molecular weight, viz.,



: judging from its properties, this latter explanation appeared the more probable. It would, perhaps, be possible to decide this question by means of the Raoult method. The compound was of a novel type, and was one of great interest. The speaker also expressed the opinion that the formula assigned to the bromindone anilide which Professor Meldola had exhibited (*Chem. Soc. Trans.*, 1890, 399) did not satisfactorily account for its colour.

Dr. Quincke drew attention to Graebe and Veillon's experiments on the oxidation of acenaphthalene and his own on nitroperinaphthaquinone; he thought that the compound obtained by the former chemists was the quinone now described by Professor Meldola and Mr. Hughes.

Mr. Groves, in reference to Dr. Armstrong's statement that the new substance was not a true quinone, remarked that the same had been said of β-napthaquinone at the time of its discovery; it was a quinone notwithstanding. The new quinone, certainly, like di-naphthlyl-β-diquinone, was very sparingly soluble in most solvents; but, on the other hand, it could easily be obtained in well-formed crystals, whilst the diquinone was a crystalline powder.

Professor Meldola stated that the limitation of the term quinone to such compounds as could be represented as diketones was quite arbitrary, and he thought it justifiable to apply the name to all four dioxy-derivatives of naphthalene indicated by theory. It was for a long time undecided whether the quinones were peroxides or diketones, and even now the question could not, in his opinion, be regarded as definitely settled. He did not think the alternative formula suggested by Dr. Armstrong was more probable than their own, but the decision of the question by Raoult's method would be attempted, although he feared the extreme insolubility of the com-

pound in most solvents would interpose great practical difficulties. The objection raised against the formula of bromindone anilide was of too general a nature to be met, especially in the absence of any alternative suggestion. He was not aware that any chemical formula could be written so as to account for the colour of an organic compound. It was well known that all the anilides of quinones were highly coloured bodies, and the formula proposed was the only one which satisfactorily represented the formation and properties of the compound in question. With respect to Dr. Quincke's observation, Professor Meldola expressed his acquaintance with the work referred to, and stated that reference had been made to it in their paper (*Chem. Soc. Trans.*, 1890, 398). The compound described by Graebe and Veillon had had the formula $C_{24}H_{14}O_2$ ascribed to it by those authors (*Ber.*, 1887, 659).

42. "The relative antiseptic powers of isomeric organic compounds." By Thos. Carnelley, D.Sc. Aberdeen, and W. Frew, Dundee.

The authors have determined the relative antiseptic powers, in reference to ordinary aerial micro-organisms, of a number of isomeric organic compounds, more particularly di-derivatives of benzene, with the object of investigating the influence of atomic arrangement on this property.

A table of results is given which indicate that, so far as the compounds which have been tried are concerned (and with the exception of the hydroxybenzoic acids), para-compounds are more antiseptic than the corresponding ortho- and meta-compounds. On the whole, compounds containing the carboxyl-group are comparatively weak, while phenols and nitro-compounds are relatively strong antiseptics; paranitrophenol being, with the exception of α-naphthol, the most powerful of any of the compounds tried. These results entirely accord with those of Walcott Gibbs and Hare, who have recently investigated the poisonous action of di-derivatives of benzene on dogs.

43. "Note on the preparation of pyrocatechol." By W. H. Perkin, Jun., Ph.D.

The very high price of pyrocatechol renders it desirable to discover improved methods of preparing it; the author has, therefore, studied the action of iodhydric acid on guaiacol, which is easily procured at a moderate cost. He finds that an almost theoretical yield of pyrocatechol may be obtained by boiling guaiacol with a fuming solution of hydrogen iodide; details are given in the paper.

44. "Benedikt's" acetyl values." (Second notice.) By J. Lewkowitsch, Ph.D.

The results quite recently brought forward by the author (these Proceedings, 1890, 72) were so unexpected that it was determined to verify them by examining other fatty acids: capric, lauric, and cerotic acids were therefore acetylated in the manner previously stated. The approximate purity of the acids used was ascertained by determining the quantity of caustic potash required for their saturation.

Capric Acid.—The acid value was found to be 318·65, while theory requires 326·2. The acetylated product gave an acid value of 176·4, and a saponification value of 350·4; consequently an acetyl value = 174.

Lauric Acid.—The acid value found was 273·02, the theoretical value being 280·5. The acetylated acid gave an acid value = 161·5, a saponification value = 293·99; its acetyl value therefore was 132·49.

Cerotic Acid.—The acid value found was 128·4; theory indicates for $C_{26}H_{52}O_2$ 141·6 (or for $C_{27}H_{54}O_2$ 136·8). The acetylated cerotic acid gave an acid value = 73·87, a saponification value = 142·1; so that the acetyl value was 68·23.

From the approximate coincidence of the acetyl value of capric acid (174) with the acid value of the acetylated acid (176·4), it might be inferred that the acetylated capric acid contains one acetyl-group, but an acid of the formula $C_{10}H_{19}O_2{\cdot}C_2H_3O$ has a theoretical acid value of 262. Similarly the value for a mono-acetyl derivative of lauric acid would be 231, and that for a mono-acetyl derivative of cerotic acid 128 (resp. 124). (The same formulæ would apply to mixed anhydrides of acetic acid and capric acid, &c.) It was easy to decide whether the action of acetic anhydride on fatty acids affected the COOH group of the latter, for in that case an alcohol of the $C_nH_{n+2}O$ series ought not to become acetylated. The author experimented on cetyl alcohol, which was treated with acetic anhydride. The acid value of the resulting substance was—as is to be expected—*nil;* the saponification value found was 192·65. As a substance of the formula $C_{16}H_{33}O{\cdot}C_2H_3O$ has theoretically a saponification value = 198, it is evident that simply etherisation of the cetyl alcohol has taken place.

It was therefore to be supposed, as the mixed anhydrides of the higher fatty acids and acetic acid could not have been formed, that by the interaction of acetic anhydride and the higher fatty acids the anhydrides of the latter had been produced—taking palmitic acid as an example—according to the following equation:—
$2C_{16}H_{31}O{\cdot}OH + (C_2H_3O)_2O = (C_{16}H_{31}O)_2O + 2C_2H_3O{\cdot}OH$. In that case the quantities of caustic potash required by the equation

$(C_{16}H_{31}O)_2O + 2KOH = 2C_{16}H_{31}O{\cdot}OK + H_2O$ ought to agree with the saponification values found. The following table gives the quantities of caustic potash required by theory, in milligrams, compared with the quantities actually used in the above experiments:—

	Mol. wt.	Theory.	Expt.
Capric anhydride $(C_{10}H_{19}O)_2O$	326	344	350·4
Lauric anhydride $(C_{12}H_{23}O)_2O$	242	294	293·99
Palmitic anhydride $(C_{16}H_{31}O)_2O$....	494	227	226·13
Stearic anhydride $(C_{18}H_{35}O)_2O$.....	550	204	221·18
Cerotic anhydride $(C_{26}H_{51}O)_2O$ ..	774	145	142
Cerotic anhydride $(C_{27}H_{53}O)_2O$...	818	137	142
Oleic anhydride $(C_{18}H_{33}O)_2O$	546	205·4	242

Considering the approximate purity of the acids used, the theoretical values agree very well with the experimental values; and it may be pointed out that with pure material it would be easy by this method to determine which is the formula of cerotic acid.

In the light of this explanation, the "acid values" found for the products of the interaction of acetic anhydride and fatty acids lose every quantitative meaning; these values have only been found as the "acetylated" acids were dissolved in cold absolute alcohol for titration with potash, which hydrolysed at once the anhydrides, hydrolysis ceasing only when a limit is reached which depends on the quantity of alcohol present, and the nature and dilution of the standard solution—in some experiments half normal soda, in others decinormal potash. Had the substances been shaken up with water (hot water does not decompose them), in the first drop of potash falling into the mixture the pink colour would have appeared at once, or very soon when the limit for the system of substances was reached. It is hardly necessary to state that experiments carried out in this direction fully bear out the correctness of the author's conclusions. Thus the interaction of KOH or NaOH and the anhydrides in aqueous solution affords an elegant illustration of that class of actions which require a measurable time for their completion. The anhydrides of the higher fatty acids are now within easy reach, as they can be prepared in a very short time by means of acetic anhydride.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

The Elements of Laboratory Work: a course of Natural Science, by A. G. Earl. London 1890. From the Publishers.

Systematic Tests for Soluble Salts, Bases, and Acids, by A. A. Sutherland. London 1889 (Pamphlet). From the Author.

The Principles of Chemistry and Molecular Mechanics, by G. Hinrichs. Davenport, U.S.A., 1874. From Hy. Bassett, Esq.

Annual Report of the Medical Officer of the Local Government Board for the Year 1888. From Dr. Buchanan.

A Guide to the Literature of Sugar, by H. L. Roth. London 1890. From the Publishers.

Histoire des parfums et hygiène de la toilette, par S. Piesse. Édition Française, par F. Chardin-Hadancourt et H. Massignon et G. Halphen. Paris 1890. Chimie des parfums et fabrication des savons, par S. Piesse. Édition Française, par F. Chardin-Hadancourt et H. Massignon et G. Halphen. Paris 1890.

From C. H. Piesse, Esq.

Geographical Survey of New South Wales :—

1. Geology of the Vegetable Creek Tin-Mining Field, by T. W. E. David. 4to. Sydney 1887.
2. Mineral Products of New South Wales, by H. Wood: Notes on the Geology of New South Wales, by C. S. Wilkinson; and Description of the Seams of Coal worked in New South Wales, by J. Mackenzie. 4to. Sydney 1887.
3. Palæontology I.—The Invertebrate Fauna of the Hawkesbury-Wianamatta Series of New South Wales, by R. Etheridge, Junr. 4to. Sydney 1888.

Annual Report of the Department of Mines, New South Wales, for the Year 1887. From the Secretary for Mines.

United States Geological Survey :—

Seventh Annual Report for 1885–6, by J. W. Powell. Washington 1888.

Monographs, Vol. XIII. Geology of the Quicksilver Deposits of the Pacific Slope, by G. F. Becker. 4to. Washington 1888.

Monographs, Vol. XIV: Fossil Fishes and Fossil Plants of the Triassic Rocks of New Jersey and Connecticut Valley, by J. S. Newberry. 4to. Washington 1888.

Bulletin. Nos. 48–53. Washington 1888–9.

From the Director of the Survey.

Grundlagen der Chemie, von D. Mendelejeff; übersetzt von L. Jawein und A. Thillot.

From Prof. Mendelejeff.

Las Aguas Minerales de Chile, por L. Darapsky. Valparaiso 1890.

From the Author.

II. *By Purchase.*

De la loi du contraste simultané des couleurs, et de l'assortiment des objets colorés considéré d'après cette loi, par E. Chevreul; avec un introduction de H. Chevreul. 4to. Paris 1889.

Die Mikro-organismen der Gährungsindustrie, von A. Jörgensen. 2te Aufl. Berlin 1890.

Traité pratique des matières colorantes artificielles derivées du goudron de houille, par A. M. Villon. Paris 1890.

Gasanalytische Methoden, von W. Hempel. 2te Auflage. 1890.

Conférences faites au laboratoire de M. Friedel. Paris 1889.

RESEARCH FUND.

Fellows desiring grants are requested to forward their applications to the Secretaries in order that they may be considered at the next meeting, early in June.

At the next meeting, on June 5th, the following papers will be read :—

"Note on the preparation of pure crystalline copper for spectroscopic work." By Mr. C. C. Duncan.

"The action of ethylic oxalate on camphor." By Dr. Bishop Tingle.

"The structure of cycloid hydrocarbons." By Dr. Armstrong.

"Studies on the constitution of tri-derivatives of naphthalene." No. 4. By Dr. Armstrong and Mr. Wynne.

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Issued 17 /6/1890.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 85. Session 1890–91.

June 5th, 1890. Dr. W. J. Russell, F.R.S., President, in the Chair.

Messrs. W. B. Shuttlewood and H. R. Kenwood were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Charles Edwin Day, 1, Merchiston Bank Terrace, Edinburgh; Robert Frost, St. James's Chambers, Duke Street, S.W.; George German, Huntingdon House, Ashby de la Zouch; Colin Gordon, Millwall Club, West Ferry Road, Millwall, E.; Frank Haydon, Ettrick, Putney Common, S.W.; Arthur E. Palmer, Ashley Mount, Tettenhall, Wolverhampton; Thomas Parkes, Grammar School, Stamford; Edward Cox Seaton, 35, George Street, Hanover Square, W.; James Mitchell Wilson, Hall Gate, Doncaster.

The following papers were read:—

45. "The production of pure metallic copper in a crystalline condition." By C. C. Duncan, King's College, London.

The method of precipitating copper oxide from a boiling solution of copper sulphate with potassium hydroxide and then reducing in electrolytic hydrogen having been found unsatisfactory, as the last traces of sulphur could not be washed away, experiments were made on the reduction of the sulphate by zinc.

To a solution containing several grams of purified sulphate made acid with hydrochloric acid, metallic zinc (containing only a trace of lead) was added in small fragments. Dark, spongy looking copper at once separated, and this soon protected the zinc from the action of

the acid; consequently the copper was very slowly deposited: it was found to be in the form of feathery, dendritic crystals.

A portion of the crystalline copper, well washed with dilute hydrochloric acid and distilled water, was dissolved in strong nitric acid free from sulphur, the solution was diluted and barium nitrate added; no precipitate of any kind formed, even after standing 48 hours, showing the absence of sulphur.

To discover whether the metallic copper contained zinc, two of the finest crystals (about 8 mm. long) were again well washed and dried in hydrogen. These crystals were then fixed in an ordinary spark-stand and the spark from a 2-inch Apps' coil, with a Leyden jar of 1 quart capacity in the circuit, was passed between them, and the light from the copper terminals was analysed by one of Browning's two-prism spectroscopes. The spectrum given by the copper was compared with that of zinc. None of the lines of zinc coincided with those given by the copper; it was therefore assumed that zinc was absent.

The bright lines given by the copper crystals agreed with those described by Thalèn ("Mémoire sur la détermination des longueurs d'onde des raies métalliques." *Act. Nova Upsal.*, iii, **6**, 1868, 29).

The spark and lines were extremely bright and no faint lines were to be seen (except the usual air-lines), showing the absence of any metallic impurity.

Microscopic examination proved the dendritic crystals to be built up of octahedrons. As the production of these crystals was quite accidental, experiments were made with different strengths of copper sulphate solutions, with and without free acid, in order to reproduce them.

In the literature relating to the reduction of metallic copper from its salts by means of metallic zinc, there is no mention whether the copper so reduced is in the crystalline state, except in a paper by Dr. Gladstone and Mr. Tribe (*Proc. Roy. Soc.*, **20**, 1872, 219), who mention the deposition of metallic copper in a crystalline condition, but they make no remark on the purity or size of the crystals so formed.

In another paper, "On the Crystallisation of Silver, Gold and other Metals" (*Proc. Roy. Institute*, **6**, 1872, 428), Dr. Gladstone again refers to crystalline copper in the following terms:—

"Copper salts give round nodules which have no crystalline appearance when deposited from moderately weak solutions, but a very strong solution of the chloride—about 40 per cent.—yields with zinc first a black, thick growth, then arborescent fringes of red metal, terminating in crystals of very appreciable size."

In all the experiments made by the author with acid and neutral copper solutions, dendritic crystals of copper were found which could

be seen with the unaided eye; they were small in the case of neutral, and large in the case of acid solutions.

The following tables give the quantity of copper sulphate, water and hydrochloric acid (rel. den. 1·152) used in the different experiments, and the results:—

	$CuSO_4$.	Water.	Acid.	Results.
I	10 grams	400 c.c.	0	Copper was at once reduced in spongy state and then in minute dendritic crystals just visible to the unaided eye. The spongy copper proved to be composed of octahedrons under the microscope. The crystals did not increase in size on standing.
II and III	20 „ / 50 „	„ / „	0 / 0	Same as I.
IV	10 „	„	10 c.c.	The dendritic crystals produced were larger than any of those in I, II and III.
V	20 „	„	10 c.c.	Same as IV.
VI	10 „	„	100 c.c.	Crystals of copper which were slightly larger than those produced in V.
VII	20 „	„	200 c.c.	Dendritic crystals of copper were produced, several of which were 10 mm. in length. Sulphur was detected in these crystals, and in most other crystals which had been reduced in a solution which was very strongly acid. No zinc was detected by the spectroscope.
VIII	40 „	„	200 c.c.	The crystals produced were only very slightly larger than those in VII, but more numerous.

As sulphur had been detected in several of the crystals deposited from the copper sulphate solutions, a few experiments were made with copper chloride free from sulphate (see table, p. 98).

Crystalline copper is said to have been obtained by using iron and aluminium as reducing agents. Thus Gore, in his text-book of "Electro-Metallurgy," pp. 203—204, refers to the use of iron in recovering copper from large deposits of the Tharsis and Rio Tinto mines in Spain. The copper is dissolved by means of hydrochloric acid, and the liquid is run into large vats filled with scrap iron. In a short time all the copper is reduced in the form of feathery crystals upon the iron. The process is described by P. Argall and G. A. Kinahan in the *Sci. Proc. Roy. Dublin Soc.*, N.S., 3, 1883, 302—328, and on p. 309 the production of crystalline copper is mentioned. No reference is made to the purity or size of the crystals.

	$CuCl_2$.	Water.	Acid.	Results.
I	10 grams	400 c.c.	0	Small dendritic crystals of copper were quickly produced. On standing the crystals increased slightly in size.
II	20 „	„	0	Numerous small dendritic crystals with several about 7 mm. long. No impurity detected.
III	10 „	„	20 c.c.	Two or three crystals about 11 mm. long with the usual mass of smaller crystals. No impurities were detected.
IV	40 „	„	20 c.c.	Four or five crystals 12 mm. long with the usual mass of smaller crystals No impurity detected.
V	140 „	500 c.c.	40 c.c.	This solution gave the finest crop of dendritic crystals yet produced. One crystal measured 15 mm., and its lateral branches were composed of clumps of crystals. The crystals were erect, and had a beautiful metallic appearance. Several of the crystals were from 5—8 mm. in length, two or three 12—13 mm., and only a little spongy copper was to be seen. No impurity could be detected. The pure crystalline copper is insoluble in pure nitric acid (free from nitrous acid). See Veley (*Proc. Roy. Soc.*, 1890).

The reduction of copper from its sulphate by the aid of aluminium is mentioned in "Watts' Dictionary of Chemistry," 2nd Sup., 1875, p. 383, in a passage which is extracted from Cossa (*Nuovo Cimento* [2], **3**, 75. The crystals of copper are described as follows:— "Aluminium foil immersed in a solution of sulphate or nitrate of copper is not acted upon at once, but after two days the foil becomes covered with crystals consisting partly of dendrites, but for the most part of well-defined octahedrons." It was found that if the solution of the copper sulphate is neutral, only octahedrons are produced; but that if an acid is present, dendrites are produced. Sulphur was the only impurity detected.

"Copper is immediately reduced by aluminium from a solution of cupric chloride, and likewise, though more slowly, from the acetate." It is not mentioned whether the copper is deposited in the crystalline or amorphous state, but the author has found on experimenting with these substances that dendritic crystals of copper are produced in both cases. No impurity could be detected.

Magnesium was found to reduce copper from a solution of copper sulphate in very small quantities, the copper being formed in small patches composed of dendrites and octahedrons. Magnesium added

to a solution of copper chloride caused an evolution of gas, throwing down a green precipitate, and at the same time reducing the copper in the spongy state. The well-washed copper contained magnesium.

In a note by M. A. Commaille "On the Action of Magnesium on Neutral Metallic Salts" in the *Chem. News*, **14**, 188, it is mentioned "that copper sulphate gives with magnesium the metal (copper), the hydrated peroxide and a green subsalt. With the chloride no metal (copper) is precipitated, but a deposit of Brunswick green."

In experiments made by the author with the chloride, copper was reduced in appreciable quantity, but in an entirely amorphous state.

46. "The action of ethylic oxalate on camphor." By J. Bishop Tingle, Ph.D.

The author finds that camphor and ethylic oxalate in presence of metallic sodium interact according to the equation $C_8H_{14}<\begin{matrix}CH_2\\|\\CO\end{matrix} + C_2H_5O{\cdot}CO{\cdot}CO_2C_2H_5 = C_8H_{14}<\begin{matrix}CH{\cdot}CO{\cdot}CO_2C_2H_5\\|\\CO\end{matrix} + C_2H_5OH$, forming *ethylic camphoroxylate*. This is an oily liquid, which decomposes on distillation; on hydrolysis it is converted into *camphoroxylic acid*, which crystallises in rhombic plates melting at 88° C. On reducing this acid with sodium amalgam, a *γ-lactone* of the formula $C_8H_{14}<\begin{matrix}CH{\cdot}CH(OH){\cdot}CO\\|\\C\text{———}O\text{——}|\end{matrix}$ is obtained, melting at 75—76°. Ethylic camphoroxylate and phenylhydrazine interact to form a *monophenylhydrazone*, which crystallises in white needles melting at 187—188° C. By the action of hydroxylamine a compound is formed which melts at 193° and will be further investigated. On heating ethylic camphoroxylate with aniline to 165°, *oxanilide* is produced.

47. "The oxidation of turpentine in sunlight." By Henry E. Armstrong.

It was pointed out by Sobrero in 1851 (*C. R.*, **33**, 66) that when turpentine is exposed to light in presence of moisture and oxygen a crystalline substance is formed which has the composition represented by the formula $C_{10}H_{18}O_2$; and that this substance is decomposed when boiled with dilute sulphuric acid, an oil being formed which has a powerful odour recalling both that of camphor and that of turpentine. The author's attention became directed to this substance about 12 years ago in the course of his studies of the terpenes and camphor, and in most years since, during the summer, he has carried

on experiments on the oxidation of $C_{10}H_{16}$ hydrocarbons in sunlight, and has been able to confirm Sobrero's statements in every particular. As the crystalline product in question has not yet been named, it is proposed to term it—at all events, provisionally and until its constitution is determined—*sobrerol*.

Sobrerol is readily soluble in alcohol, and crystallises from this solvent usually in large, flexible, monosymmetric prisms having a peculiar hour-glass structure inside and showing hemihedrism. It is slightly soluble in water, benzene, chloroform and petroleum spirit; the aqueous solution has a bitter taste. It melts at about 150°. The results obtained on analysis (carbon, 70·57 and 70·49 per cent.; hydrogen, 10·71 and 10·74 per cent.) show that, as Sobrero states, it has the formula $C_{10}H_{18}O_2 = C_{10}H_{16} + H_2O_2$, and there can be very little doubt that it is a glycol; but, owing to its extreme sensitiveness to the action of acids, it is difficult to prove this by the ordinary methods. Sobrerol is optically active in a high degree, the apparent specific rotatory power of the products from French turpentine in a 5 per cent. solution in alcohol (B. P.) being slightly above 150°. Sobrerol from American turpentine (from Savannah) was found to have about the same rotatory power, but in the opposite direction. The optical similarity of the two products is noteworthy, inasmuch as the American has less than half the rotatory power of French turpentine. It would seem that only the terpenes proper, and not the citrenes, &c. (*cf. Chem. Soc. Trans.*, 1879, 734; *J. Soc. Chem. Ind.*, 1882, 478) form sobrerol. To ascertain whether this be the case, and what are the crystallographic and optical relationship of the products obtained from terpenes from different sources, the author is engaged in conjunction with Mr. W. J. Pope—to whom he is indebted for assistance in the research—in studying the behaviour of pure $C_{10}H_{16}$ hydrocarbons of all kinds.

When boiled with dilute sulphuric acid, sobrerol is readily converted into the oil referred to by Sobrero; the product is undoubtedly identical with the isomeride of camphor which Wallach and Otto have obtained by treating turpentine with nitrous acid (*Annalen*, **253**, 249), and which they have provisionally named *pinol;* as the compound is not an *ol*, *i.e.*, an alcohol, it may be suggested that it might appropriately be termed *sobrerone*. The product from sobrerol begins to boil at 150—160°, but passes over almost entirely at about 183°, leaving a small amount of a viscid oil; it readily combines with bromine, forming a dibromide (bromine found 50·78 per cent.) which crystallises very beautifully in forms of the rhombic system, the lengths of the axes being in the ratio $a : b : c = 0{\cdot}5696 : 1 : 1{\cdot}5553$, dimensions which almost absolutely agree with those quoted by Wallach and Otto, viz., $a : b : c = 0{\cdot}5700 : 1 : 1{\cdot}5553$. The di-

bromide was found to melt at 93·5°, 94° being the melting point given by Wallach and Otto.

The formation of sobrerone from sobrerol is of interest as serving to explain its formation by Wallach and Otto's method: very probably sobrerol is first produced, and is at once acted on by the acid. Sobrerol is probably always the initial product of oxidation of turpentine. It may be expected that sobrerone will be found among the oxygenated constituents of some essential oils, and it is proposed to search for it.

If, as appears probable, sobrerol be a glycol, the formation of sobrerone from it is analogous to that of pinacolin from pinacone; but, in this latter case, an isomeric change takes place, pinacolin being a ketone, $CMe_3 \cdot CO \cdot CH_3$, and not the oxide corresponding to pinacone. Wallach and Otto's observations, however, show that sobrerone is not a keto-compound. It would, therefore, appear to follow that sobrerone is an oxide formed by withdrawal of the elements of a water molecule from two hydroxyls attached to contiguous carbon atoms.

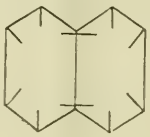
48. "The structure of cycloid hydrocarbons." By Henry E. Armstrong.

The appearance of Bamberger's remarkable papers (*Annalen*, **257**, 1; *Ber.*, 1890, 1124), in which formulæ are proposed for naphthalene, anthracene, &c., apparently analogous to that suggested by v. Baeyer and the author for benzene, renders it desirable that the cases in which this formula is applicable should be carefully considered, especially as the somewhat novel conceptions which the author would associate with this symbol tend to limit the extension of the hypothesis.

Although superior to all other symbolic expressions in almost every respect, Kekulé's formula is, nevertheless, admittedly open to the objections (1) that it apparently involves the existence of two ortho- and two meta- di-derivatives; and (2) that it represents benzene as containing three pairs of carbon-atoms in the condition of those in ethylene. The *centric* formula was developed to meet these objections. It represents benzene as a symmetrical configuration, and is suggestive of only three di-derivatives. The six affinities which in Kekulé's symbol act in pairs, as in ethylene, are assumed actually to neutralise each other much as the affinities do in paraffins, but without constituting cross linkages within the ring as represented in the Claus formula, for example: the behaviour of the hydroterepthalic acids, of quinone and of anthracene, and, among others, Kekulé's researches on the constitution of pyridine, of which he recently gave an account

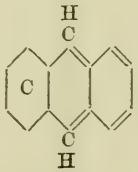
in Berlin, affording, in the author's opinion, abundant evidence of the non-existence of such cross linkages. The conception in his mind, to which, however, expression has not hitherto been given, has always been that the centric affinities act within a cycle rather than merely towards the centre in the manner pictured, and that there are peculiarities in the carbon-atom which render such a form of action possible: benzene, according to this view, may be represented by a double ring, in fact. It would appear that when an additive compound is formed the inner cycle of affinity suffers disruption, and, such a cycle being no longer possible, the contiguous carbon-atoms to which nothing has become attached of necessity acquire the ethylenic or unsaturated condition.

An extension of the hypothesis to naphthalene was suggested in September last year in a paper read at the British Association meeting at Newcastle (*B. A. Report*, 1889, 175). The following is the symbol there proposed:—



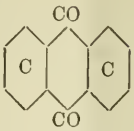
This symbol again involves the admission of the unusual conception that an affinity can act in two directions (*cf. Phil. Mag.*, June, 1888), the two carbon-atoms common to the two nuclei being represented as exerting an influence in both nuclei. In this case also the "centric" affinities are regarded as acting within a cycle composed, however, of 10 carbon-atoms; but no separation of the central carbon-atoms, such as Bamberger suggests, is supposed to have taken place. It becomes possible in this hypothesis, in a measure, to understand that a radicle in the one nucleus should, as is known to be the case, exercise an influence on a radicle in the other nucleus.

It appears to have hitherto been supposed that anthracene has a symmetrical structure: the author contends, however, that this is not the case, and that it is to be represented by the formula



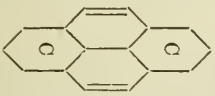
wherein C is the centric nucleus of benzene; but anthraquinone — which, strictly speaking, is derived from dihydroanthracene and not

from anthracene—is symmetrical and contains two centric benzene nuclei, thus :—



The behaviour of anthracene and anthraquinone appears to be entirely in accordance with these conclusions. Phenanthrene may be regarded as composed of two lateral "centric" nuclei, to which is conjoined a median nucleus in which the only two "available" carbon-atoms are in the ethylenic condition.

The behaviour of anthracene is more nearly that which it may be supposed the hypothetical hydrocarbon having the structure indicated by Kekulé's benzene symbol would manifest. Pyrene, probably, is still more closely related to the ethylenic form of benzene, and has little, if any, resemblance to the centric form. Two formulæ may be assigned to this hydrocarbon—



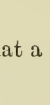
The first of these is the symbol of a phenanthrene derivative, but the behaviour of pyrene is so entirely unlike that of phenanthrene that it may be regarded as out of the question ; the second would appear to be entirely in accordance with the results of Bamberger's researches.

It is contended that the formulæ now suggested serve to explain the exceptional physical properties of hydrocarbons such as anthracene and pyrene.

Discussion.

Dr. Japp desired to know what precise mechanical conception Dr. Armstrong wished to express by the broken bonds in his centric formula. They appeared to denote attractive forces which stopped half-way—in other words, attractive forces which did not attract. In this way the centric formula would resolve itself into a benzene hexagon with triadic carbon.

Professor Ramsay said that he did not see the necessity of substituting an unusual conception for the one in common use, which, in his opinion, gave a sufficient and clear mental picture of the relations between benzenoid compounds. In the case of crotonic and isocrotonic acids, an isomeric change is known whereby the position of the "double bond" is shifted. The difficulty in unreservedly accepting

Kekulé's benzene formula, caused by the fact that two ortho-compounds are unknown, while they are required by his conception, was, to some extent, removed by Kekulé himself by his supposition that the double bonds were not stationary but were sometimes between carbon-atoms 1 and 2, and sometimes between 2 and 3. In order to explain the fact that a change from the symbol  to the symbol is possible, it may be conceived that so long as no external influence is exerted on the benzene ring, it has the constitution suggested by Kekulé. It is probable that two isomeric ortho-compounds are impossible, because, if formed by substitution of hydrogen-atoms 1 and 2, a change would take place whereby the double bond, connecting 1 with 2, would be dissolved and replaced by a single bond, while the double bonds would then exist between 1 and 6, 3 and 2 and 5 and 4. Or the contrary may be the case, and the single bond may be the more unstable form of union, in which case, if an ortho-compound were formed between 2 and 3, the position of the bonds would also be reversed. The case of a change of position of double bonds in the crotonic acids renders this hypothesis not untenable.

Mr. Crompton agreed with Professor Ramsay in his remarks, and thought that objections to the Kekulé symbol, based on the view that, because this symbol contained double bonds, benzene should behave as an olefinic compound, were unjustifiable. A double bond was nothing more than an incomplete representation, on paper, of an unsaturated condition or want of equilibrium in the molecule, a state of things that might be due to totally different and distinct causes in the two cases. The behaviour of benzene in this respect must, therefore, differ from that of ethylene. The difference would have to be looked for in the different configurations of the molecules; but it was just this point that received no representation, or only an inadequate one, in the plane formulæ at present in use. The problem would, no doubt, only be finally solved when satisfactory space formulæ for these compounds had been discovered.

In reply to Dr. Japp, Dr. Armstrong said that the broken bonds were intended to figure as resultants, much as the conjoined effect of two forces acting from different directions was expressed by their resultant. Referring to Professor Ramsay's remarks, he expressed the opinion that the isomerism of the crotonic acids was not sufficiently understood to serve as an argument in such a case. However

well the non-existence of isomeric ortho- and meta-derivatives might be accounted for by Kekulé's oscillation hypothesis, it was impossible in this way to explain the fact that benzene, on the whole, behaved as a saturated and not as an ethylenic compound; there was also no reason to suppose, as Mr. Crompton had suggested, that "double bonds" in a ring would behave differently from those in an open chain: the whole of v. Baeyer's recent work was in contradiction to any such assumption, and Thomsen's and other observations left little doubt that in the formation of benzene there is a considerable "outgoing of affinity" beyond that which takes place when ethylenic union is effected. He scarcely thought that the introduction of geometric considerations would materially advance the solution of the problem under discussion. Whatever the ultimate fate of his hypothesis, he was convinced that a settlement of many practical problems —those relating to laws of substitution and isomeric change, for example—required the knowledge of the inner structure of the cycloid hydrocarbons; and such speculations, even if proved to be entirely false, at least served to suggest fresh lines of experimental inquiry, and on this account were not only permissible but also desirable.

49. "Tertiary butyl mercaptan." By Leonard Dobbin, Ph.D., Chemical Laboratory of the University of Edinburgh.

The author finds that when tertiary butyl iodide is digested at a gentle heat with a sufficient quantity of zinc sulphide, an interaction takes place which results in the formation of tertiary butyl mercaptan. It is a colourless, extremely volatile liquid which boils at 65—66°, possessing an overpowering and disagreeable smell, recalling that of other mercaptans; it solidifies in a freezing mixture of snow and salt to a white, semi-translucent mass; it forms white, insoluble compounds with mercuric chloride and with silver nitrate.

Products of higher boiling point are formed at the same time as the mercaptan; these are believed to be tri-isobutylene, and probably also tertiary butyl sulphide. This part of the subject is under investigation.

50. "Desylacetophenone." By Alex. Smith, B.Sc., Ph.D., Chemical Laboratory of the University of Edinburgh.

The author finds that a dilute solution of potassium cyanide in alcohol and water acts in many cases as a condensing agent. By boiling equimolecular proportions of benzoin and acetophenone in dilute alcohol with very little potassium cyanide, a condensation product, *desylacetophenone*, is formed, $C_6H_5{\cdot}CO{\cdot}CH(C_6H_5)(OH) + CH_3{\cdot}CO{\cdot}C_6H_5 = C_6H_5{\cdot}CO{\cdot}CH(C_6H_5){\cdot}CH_2{\cdot}CO{\cdot}C_6H_5 + H_2O$, which is

the saturated compound corresponding to Japp's anhydracetophenonebenzil. It may be got perfectly pure and white by recrystallisation from acetic acid and alcohol. It melts at 126°. It is easily transformed into *triphenylfurfurane*, *triphenylpyrrole* and *triphenylthiophen*, showing its constitution to be that given above. It forms a mono- and a di-hydroxime; by its interaction with one molecular proportion of phenylhydrazine, two molecular proportions of water being given off, an oiazine (pyridazine) is formed. This latter compound is converted by excess of phenylhydrazine into $\alpha\alpha'\beta$-N-tetraphenylpyrrole.

A large quantity of another substance having the formula $C_{29}H_{22}O_2$ is formed at the same time as the desylacetophenone. It would seem that the benzoin, or a part of it, acts as benzaldehyde, $3C_6H_5{\cdot}COH + CH_3{\cdot}CO{\cdot}C_6H_5 = C_{29}H_{22}O_2 + 2H_2O$.

From *acetone* and benzoin the only substance isolable, if not, indeed the only one formed, is that corresponding to the last-mentioned product from acetophenone. It has the formula $C_{24}H_{20}O_2$. The properties and constitutions of these two substances are still under investigation; as are also some other applications of the new interaction.

At the next meeting, on June 19th, there will be a ballot for the following candidates:—

1. Branson, Charles F., Kenly Lodge, Macaulay Road, Clapham Common.
2. Edward, John Hutchison, 117, Stockport Road, Manchester.
3. Haslam, Arthur R., Ph.D., 64, Rathgar Road, Dublin.
4. Jenkins, Wallis, 410, Glossop Road, Sheffield.
5. Johnson, John Robert, 16, Oxford Street, Liverpool.
6. Kelly, Patrick, 43, Lennox Street, Dublin.
7. McKillop, John, Pulan Brani, Singapore.
8. Parker, Thomas, M.I.C.E., Wolverhampton.
9. Redding, Richard James, Royal Laboratory, Woolwich Arsenal.
10. Smith, Frederick, Johannesburg, Transvaal, South Africa.
11. Thornley, John Brooks, Ivanhoe Terrace, Ashby-de-la-Zouch.

The following papers will be read:—

"Invertase, a contribution to the history of an unorganised ferment." By C. O'Sullivan, F.R.S., and F. W. Tompson.

"The action of carbonic oxide on nickel." By Mr. Mond and Drs. Langer and Quincke.

"The interaction of iodine, water and potassium chlorate." By H. Bassett.

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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 86. Session 1890–91.

June 19th, 1890. Dr. W. J. Russell, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. J. Caird, 20, Springfield, Dundee; D. G. Clark, 44, St. John's Wood Park, N.W.; Walter Henry Coleman, 41, Poynings Road, Junction Road, N.; Thomas Rhymer Marshall, 4, East Castle Road, Edinburgh; William Alexander McCubbin, Mill Bank House, West Derby, Liverpool; William Stagg, 52, Seymour Road, Bristol.

Of the following papers, those marked * were read:—

*51. "Invertase: a contribution to the history of an enzyme or unorganised ferment." By C. O'Sullivan, F.R.S., and Fred. W. Tompson.

The substance present in yeast, &c., known as *invertase*, which possesses the power, under suitable conditions, of inducing the hydrolysis of cane-sugar, has been studied by the authors with the object of determining the precise manner in which it acts and its constitution.

The method adopted in determining the functions of invertase is essentially that developed by Vernon Harcourt in his paper "On the observation of the course of chemical change." A solution of cane-sugar was mixed with a measured amount of invertase, and the action was allowed to take place at a known temperature during a definite time; action was then stopped by the addition of alkali, and its extent determined.

The authors arrive at the following conclusions:—

1. The rate of hydrolysis of cane-sugar by means of invertase may always be expressed by a definite time-curve; this curve is practically that given by Harcourt as expressing a chemical change "of which no condition varies excepting the diminution of the changing substance." There are, however, some slight and apparently constant deviations from the theoretical curve.

2. Whatever the conditions may be under which hydrolysis is taking place, as long as these conditions remain unchanged, this curve is adhered to.

3. When the degree of acidity is that most favourable for the action of invertase, the rapidity of the action is in proportion to the amount of invertase present.

4. The most favourable concentration of the sugar solution at a temperature of 54° C. is about 20 per cent. Below that there is a rapid decline in the speed of hydrolysis. Greater concentrations are only slightly less favourable until about 40 grams per 100 c.c. is reached. In saturated solutions hydrolysis only proceeds with extreme slowness.

5. The speed of hydrolysis increases rapidly with the temperature until 55—60° C. is reached. At 65° C. the invertase is slowly destroyed, and at 75° C. it is immediately destroyed. At the lower temperatures the speed of the action increases with rise of temperature in accordance with Harcourt's law: the rate being about doubled for 10° rise; but above 30° C. the increase is not nearly so rapid.

6. Elevated temperatures have no permanent effect on the activity of the invertase so long as they are not sufficiently high to destroy it.

7. The caustic alkalis, even in very small proportions, are instantly and irretrievably destructive of invertase.

8. Minute quantities of sulphuric acid are exceedingly favourable to the action, but a slight increase of acidity beyond the most favourable point is very detrimental. The most favourable amount of acid increases to some extent with the proportion of invertase, and decreases with rise of temperature, but the authors have not been able to discover on what it depends.

9. In studying the action of invertase it is of the utmost importance that the most favourable amount of acid should be employed; otherwise correct results cannot be obtained. At a temperature of 60° C. the action is almost stopped unless exactly the right amount of acid is used, whilst if this factor is properly adjusted hydrolysis proceeds at (probably) the maximum speed.

10. The influence of alcohol varies in direct proportion with the amount present. 5 per cent. of alcohol decreases the speed of the action by about one-half.

11. The dextrose formed by the action of invertase is initially in the birotary state.

12. The optical activity of a solution undergoing hydrolysis is no guide to the amount of hydrolysis that has taken place.

13. If a caustic alkali be added to a solution undergoing hydrolysis, and the optical activity be allowed sufficient time to become constant, it is a true indicator of the amount of inversion that had taken place at the moment of adding the alkali.

14. A sample of invertase which had induced hydrolysis of 100,000 times its own weight of cane-sugar was still active.

15. Invertase itself is not injured or destroyed during its action on cane-sugar.

16. There is no limit to the amount of sugar which can be hydrolysed with the aid of invertase.

17. The hydrolysis of cane-sugar by means of invertase is a simple chemical change differing in no important way from those which inorganic substances undergo.

18. The products of hydrolysis have no influence on the rate of the action.

19. A solution of invertase will withstand a temperature 25° C. higher in the presence of cane-sugar than in its absence.

20. The authors are of opinion that when invertase inverts cane-sugar combination takes place between the two substances, and that the invertase remains in combination with the invert-sugar. This combination breaks up in the presence of molecules of cane-sugar.

21. A means of estimating the activity of a material containing invertase has been devised which consists in recording the result by means of the time factor $\pm 0 = x$ min. In this equation $\pm 0 =$ a certain definite amount of work and $x =$ the time necessary to perform it. The expression means that the given inverting material takes x minutes to invert a standard amount of cane-sugar under standard conditions. The number x varies in inverse proportion to the actual amount of invertase contained in the material or materials under examination.

22. If sound brewers' yeast be pressed and then kept at the ordinary temperature for a month or two, it does not undergo putrefaction, but changes into a heavy, yellow liquid; the product possesses no power of fermentation, but an apparent increase takes place in the invertive power.

23. From such liquefied yeast it is easy to filter off a bright solution of high hydrolytic power. It is shown that all the invertase of the yeast is in this solution, which is termed yeast liquor.

24. Yeast liquor has a relative density of about 1080. It will re-

main for a long time unaltered, excepting that the colour darkens. If exposed to the air it may slowly become covered with mould.

25. If spirit be added to yeast liquor until the mixture contains 47 per cent. of alcohol, the whole of the invertase separates with only a slight loss of power. This precipitated invertase may be washed with spirit of the same strength and then the residue either dehydrated with strong alcohol and dried *in vacuo*, or else it may be extracted by means of 10 to 20 per cent. alcohol and then filtered. The filtrate contains the invertase. On one occasion the extent of the loss involved by this process was determined and it was found that all the invertase of the yeast liquor was present in the filtrate except 12·3 per cent.

26. The authors have not succeeded in further purifying invertase preparations carefully made in this manner. The slightest attempt at purification destroys the invertase.

27. They have prepared invertase almost free from ash.

28. The inverting power of pressed English yeast varies from $0 = 1000''$ to $\pm 0 = \pm 3000''$, or about $\frac{1}{3}$ of these amounts if calculated on the dry solid matter of the yeast.

29. The inverting power of the most active invertase preparation made was $\pm 0 = 25{\cdot}1$ on the dry solid matter. It is believed that pure invertase would approximately have $\pm 0 = 22{\cdot}5$ min.

30. The dry solid matter of yeast contains from 2 to 6 per cent. of invertase. 5·8 per cent. of invertase was separated from one sample of yeast.

31. During the preparation of invertase from yeast liquor an albuminoid is obtained, which is not redissolved by water. This is termed yeast albuminoid.

32. Invertase when it approaches a pure state is a very unstable substance. The products of its decomposition have been carefully examined and are found to constitute a new series of substances belonging to *the invertan series*.

33. The invertan series is a homologous series of substances which on analysis yield numbers which may be expressed in terms of an albuminoid and a carbohydrate. Seven members of the series are described.

34. The authors consider that invertase itself is a member of the invertan series, and call it β-invertan.

35. If the products of the decomposition of β-invertan are examined, it is usually found that they consist of α- and δ-invertan. The former contains more, and the latter less, nitrogen than invertase.

36. α-Invertan is insoluble in water, and in all its other properties seems to resemble yeast albuminoid. It contains 8·35 per cent. N. It is a very stable substance.

37. β-Invertan or invertase is soluble in water, and is the only member of the series which has the power of inverting cane-sugar. It contains about 3·69 per cent. N, and its optical activity is $[\alpha]_j = + 80°$ (?).

38. γ- and δ-Invertan are the products of the simplification of invertase. One or other of these two substances seems invariably to be formed. They both contain less nitrogen than invertase, and are always accompanied by α-invertan. Both are readily soluble in water. They contain respectively 3·15 and 2·43 per cent. N, and their optical activity is $[\alpha]_j = + 45°$ and $+ 54°$.

39. ϵ-Invertan is formed from the slow breaking down of δ-invertan. At the same time an insoluble substance, resembling α-invertan, is formed. This probably consists of another member of the series coming between α- and β-invertan. ϵ-Invertan is soluble in water, and has $[\alpha]_j = + 65°$. It contains 2·07 per cent. N.

40. ζ-Invertan results from the splitting up of ϵ-invertan in the same way that the latter is formed from δ-invertan. Its optical activity is $[\alpha]_j = + 75°$, and it yields 1·61 per cent. N.

41. η-Invertan is formed by the action of boiling sulphuric acid on ζ-invertan. It contains less nitrogen than the latter substance, but the substance has not yet been sufficiently investigated to give reliable figures.

42. The further products of the action of sulphuric acid on ζ-invertan are two soluble substances, one containing a considerable amount of nitrogen, and the other with little or no nitrogen, a high cupric reducing power and a low (dextrorotatory) optical activity.

43. The properties of all the members of the series, except α-invertan, are very similar. They are all soluble in water, forming bright solutions, which do not cloud on boiling. They are all readily thrown out of solution by alcohol, provided a little acid is present; the precipitates so formed are transparent colourless syrups, miscible with water in all proportions. The solutions are all dextrorotatory.

44. All the members of the invertan series, except η-invertan, yield a pink coloration on boiling with Millon's reagent.

45. All the members of the invertan series, except α-invertan, when submitted to the action of an alkaline copper solution, readily yield a very characteristic copper compound, from which the invertan (except β-invertan) may be separated unaltered. Invertan can probably form several such copper compounds, all having a similar appearance, but affording different percentages of copper oxide.

46. In the presence of a very large excess of alkali, a copper compound is also formed from α-invertan, but on examination it is found that the α-invertan has been split up into an albuminoid and ζ-invertan, the copper compound being that of ζ-invertan.

47. It is believed that the members of the invertan series are combinations of yeast albuminoid with η-invertan, and that yeast albuminoid itself is probably a combination of yeast albuminoid with a carbohydrate.

48. According to this theory the composition of the carbohydrate present in the invertan series, calculated from the average of all the analyses, would be C = 43·22 per cent. and H = 6·28 per cent. These numbers agree very closely with those required by a hypothetical carbohydrate coming midway between the *in* and the *on* groups.

49. It is thought that η-invertan contains 18 parts by weight of this carbohydrate to 1 of albuminoid, and that α-invertan contains 3 parts of the carbohydrate to 4 of albuminoid.

59. The other members of the series are formed by the union of these two substances according to the general formula $\eta + \alpha_n$, where η represents η-invertan and α represents α-invertan. In this way we look upon invertase (β-invertan) as $\eta\alpha_5$. This splits up into α- and γ-invertan according to the formula $\eta\alpha_5 = \eta\alpha_4 + \alpha$. $\eta\alpha_4$ represents γ-invertan, and this may be further transformed by elimination of α into $\eta\alpha_3$, or δ-invertan.

60. The numbers calculated for the constitution of the above theoretical homologous series agree with considerable closeness with those obtained from the analysis of members of the invertan series.

61. The number obtained from a single determination by Raoult's freezing process for the molecular weight of ζ-invertan is considerably less than the possible molecular weight of ζ-invertan, according to the authors' theory of its constitution.

*52. "The action of carbon monoxide on nickel." By Ludwig Mond, C. Langer, Ph.D., and F. Quincke, Ph.D.

When carbon monoxide is passed over finely-divided nickel, such as is obtained by reducing nickel oxide by hydrogen at about 400°, at a temperature between 350° and 450°, carbon dioxide is formed, and the nickel is gradually converted into a black, amorphous powder, consisting of carbon and nickel; the composition of this deposit varies widely with temperature and time. A small quantity of nickel can thus change a very large amount of carbon monoxide, the action being complete and rapid at first, and continuing, although at a diminishing rate, for several weeks. A product containing as much as 85 parts carbon to 15 parts nickel has been obtained. Acids only partially remove the nickel; the carbon is very readily acted on by steam, carbon dioxide and hydrogen without a trace of carbon monoxide being formed at a temperature of 350°.

On allowing the substance to cool in a current of carbon monoxide,

it was noticed that the flame of a Bunsen burner into which the escaping gas was introduced became luminous, and when the tube through which the gas passed was heated, a deposit of nickel, mixed with a small quantity of carbon, was obtained. The authors were thus led to discover the existence of a volatile nickel compound.

To prepare this compound, a combustion-tube is filled with nickel oxide and this is reduced by hydrogen at about 400°; after cooling the nickel to about 100°, pure dry carbon monoxide is passed over it without further heating, and the issuing gas is led through a tube placed in a freezing mixture: the major portion of the nickel compound condenses as a colourless liquid, but the gas retains about 5 per cent., and is therefore collected, dried and again passed over the metal. When no more liquid condenses, the nickel is again heated to about 400° in a slow current of pure carbon monoxide; it is then cooled to about 100°, and again submitted to the action of the gas.

Nickel carbonoxide thus prepared is a colourless liquid, which boils at 43° under 751 mm. pressure; its relative density at 17° is 1·3185. It solidifies at — 25° to a mass of needle-shaped crystals. Its composition is represented by the formula $Ni(CO)_4$. It dissolves in alcohol, and more readily in benzene and chloroform; dilute acids and alkalis have no action on it, but it is oxidised by concentrated nitric acid. It reduces an ammoniacal solution of cupric chloride, and it also causes the separation of silver from an ammoniacal solution of silver chloride. It interacts with chlorine, forming nickel chloride and carbon oxychloride. It is decomposed at 180° (in boiling aniline vapour) into nickel and carbon monoxide. The atomic weight of the deposited metal was found in three experiments to be 58·52—58·64, a result closely corresponding with Russell's value, 58·74.

Numerous experiments to obtain similar compounds with other metals, notably with cobalt, iron, copper and platinum, led to negative results. On experimenting with specially purified cobalt, in the beginning a slight coloration of the Bunsen flame into which the gas was led was noticed, but after a time this was no longer observed. Commercial cobalt afforded a gas which deposited a mirror of pure nickel, it being possible, in fact, to purify cobalt from nickel by carbonic oxide. The nickel mirrors obtained by heating the carbonic oxide compound do not appear to contain any trace of cobalt.

*53. "The interaction of iodine, water and potassium chlorate." By Henry Bassett.

The author finds that the usual statement that the chlorine in potassium chlorate is directly displaced by iodine when subjected to treat-

ment in accordance with Millon's directions is incorrect; he considers that the evolution of chlorine observed by Millon is due to a secondary interaction, $HIO_3 + 5HCl = 3H_2O + ICl + 2Cl_2$, which takes place when the iodine is added all at once, and is due doubtless to the rapid formation of iodic acid and hydrogen chloride within the dense mass of iodine. His experiments show that the iodate is formed in accordance with the equation $6I_2 + 10KClO_3 + 6H_2O = 6KHI_2O_6 + 4KCl + 6HCl$; and that on evaporating the solution to dryness on the water-bath, decomposition of a portion of the biniodate takes place: $KHI_2O_6 + 12HCl = KCl + 6H_2O + ICl + ICl{\cdot}HCl + 4Cl_2$.

*54. "The milk of the Gamoose." By A. Pappel and H. D. Richmond, Khedival Laboratory, Cairo.

The milk of the Egyptian gamoose or buffalo (*Bos Bubalus*) is distinguished from that of the cow by its white colour and peculiar musk-like smell. The authors find the average composition to be as follows:—

Water	84·10		
Fat	5·56		
Sugar	5·41		
Casein	3·26	containing N	0·511
Albumin	0·60	„ „	0·094
Nitrogen bases	0·09	„ „	0·035
Salts	1·03		

The fat was found to vary from 7·35 to 5·15 per cent., and the solids not fat from 10·67 to 10·07 per cent. The average relative density at 15·5° was 1·0354; the increase in eight hours after milking was 0·0006, and in 24 hours 0·0007. Gamoose milk, therefore, differs from that of the cow, both in the high percentage of fat and of solids not fat, the increase in the latter being largely due to the sugar.

Comparing the fat with that of cows' milk, the chief differences noted by the authors are, (1) the presence of small quantities of sulphur and phosphorus; (2) the presence of fatty acids soluble in boiling water but not volatile in much larger amount than in cows' milk; (3) the presence of fatty acids giving lead salts soluble in ether but not members of the oleic series; (4) the difference in the ratio between caproic and butyric acid—4 : 1 instead of 2 : 1. Other alcohols than glycerol do not appear to be present.

The sugar appears not only to be different from milk sugar, but novel, its rotatory power being $[\alpha]_D = 48{\cdot}7$, and its cupric-reducing power $\kappa = 73{\cdot}7$; it yields only dextrose on hydrolysis. It is proposed to name it *tewfikose*.

The authors also state that the milk contains a small amount of citric acid.

55. "The action of heat on the chlorides and hydroxides of mixed quaternary ammonium compounds." By N. Collie, Ph.D., and S. B. Schryver, B.Sc.

The object of the author's experiments has been to devise, if possible, a general method for preparing mixed tertiary amines. One of them (Collie, *Chem. Soc. Trans.*, 1888, 714—726) has shown that mixed tertiary phosphines could be prepared by heating the quaternary phosphonium compounds, and the following results show distinctly a marked analogy between the compounds of nitrogen and those of phosphorus.

Hofmann has already pointed out that when the hydroxides of mixed quaternary ammonium compounds containing ethyl are heated, one of the ethyl groups is invariably eliminated in the form of ethylene, *e.g.*, $(C_2H_5)_3(C_5H_{11})N{\cdot}OH = (C_2H_5)_2(C_5H_{11})N + C_2H_4 + H_2O$; and Lossen has obtained similar results. But none of the mixed tertiary amines were thus prepared in a state of purity; both Hofmann and Lossen were content to reconvert the products into quaternary ammonium chlorides and analyse the platinum salts. The authors have used trimethylamine and triethylamine, and from these tertiary amines have prepared the quaternary ammonium compounds by heating the alcoholic solution of the amine with the iodide or chloride of primary, secondary or tertiary hydrocarbon radicles of the C_nH_{2n+1} series. The action of heat on the quaternary ammonium compounds containing the radicles allyl, benzyl and phenyl has also been studied. The mixed tertiary amines which have thus been prepared for the first time in the pure condition are:—

Dimethylethylamine,	b. p.	45—46° C.
Diethylmethylamine	,, ...	66—67° C.
Dimethylamylamine	,, ...	113—114° C.
Dimethylbenzylamine	,, ...	178—179° C.

56. "Action of phosphoric anhydride on fatty acids." By F. Stanley Kipping, Ph.D., D.Sc.

The investigation of the action of phosphoric anhydride on fatty acids has now been extended to palmitic acid and lauric acid, and some preliminary experiments have also been made with caproic acid. These compounds, like stearic acid and heptylic acid, are decomposed by phosphoric anhydride at a moderately high temperature in accordance with the equation $2R{\cdot}COOH = R_2CO + CO_2 + H_2O$. As the

ketone produced can easily be obtained in a pure condition and the yield is also good, this method may be conveniently employed for the preparation of the compounds in question.

Palmitone, $(C_{15}H_{31})_2CO$, can be prepared by heating palmitic acid at 200—210° and gradually adding a slight excess of the theoretical quantity of phosphoric anhydride. The dark-brown mass is allowed to cool, treated first with water and then with soda to free it from phosphoric acid, and the residue extracted several times with boiling alcohol; on cooling, the ketone separates from the alcoholic extracts as a yellowish powder and can be obtained in a pure condition by recrystallising it from boiling alcohol. The yield of the pure product is more than 50 per cent. of the theoretical. It is a colourless, crystalline powder melting at 82—83°. The *hydroxime*, $(C_{15}H_{31})_2C{:}N{\cdot}OH$, forms peculiar fern-like crystals and melts at about 64—65°.

Dipalmitylcarbinol, $(C_{15}H_{31})_2CH{\cdot}OH$, is obtained by reducing palmitone with sodium in boiling alcoholic solution; it crystallises from alcohol in silky plates and melts at 84—85°. When boiled with acetic anhydride for several hours, it is converted into a colourless, crystalline *acetyl*-derivative, $(C_{15}H_{31})_2CH{\cdot}OAc$, melting at 49—50°.

Laurone, $(C_{11}H_{23})_2CO$, can be easily prepared by heating lauric acid at 220—230° with a slight excess of the theoretical quantity of phosphoric anhydride; at a lower temperature the acid is not readily decomposed. The product is purified as described in the case of palmitone; the yield is about 40 per cent. of the theoretical. The *hydroxime*, $(C_{11}H_{23})_2C{:}N{\cdot}OH$, is formed when the ketone is heated with hydroxylamine hydrochloride and excess of potash in dilute alcoholic solution; it crystallises from alcohol in slender needles and melts at 39—40°.

Dilaurylcarbinol, $(C_{11}H_{23})_2CH{\cdot}OH$, is obtained when the ketone is reduced with sodium and water in ethereal solution; it crystallises in colourless, waxy plates and melts at 75—76°. The *acetyl*-derivative, $(C_{11}H_{23})_2CH{\cdot}OAc$, is formed when the alcohol is boiled with acetic anhydride for some hours; it crystallises from methyl alcohol in colourless plates melting at 34—35°.

Caproic acid, at its boiling point, is decomposed by phosphoric anhydride, giving the ketone $(C_5H_{11})_2CO$; the product can be isolated by distillation with steam. The yield seems to be fairly good.

57. "$\alpha\alpha'$-Dimethyl-$\alpha\alpha'$-diacetylpentane." By F. Stanley Kipping, Ph.D., D.Sc., and J. E. Mackenzie, B.Sc.

The conversion of $\alpha\alpha'$-diacetylpentane into dimethyldihydroxyheptamethylene on reduction (Kipping and Perkin, Proc., 1889, 145)

being an action to which much interest attaches, the authors have instituted experiments with a view to ascertain whether other diketones of analogous constitution can be converted into heptamethylene-derivatives in a similar manner. The investigation is not yet completed, but *αα′*-dimethyl-*αα′*-diacetylpentane and various other compounds have already been prepared.

Ethylic αα′-dimethyl-αα′-diacetylpimelate, $C_3H_6(CMeAc\cdot CO_2Et)_2$, can be obtained by treating ethylic methylacetoacetate with trimethylene bromide and sodium ethoxide in absolute alcoholic solution; a considerable quantity of compounds of lower boiling point is also formed, so that the yield of ethylic dimethyldiacetylpimelate is only 50—60 per cent. of the theoretical. It is a colourless oil boiling at about 250° under a pressure of 60 mm. On hydrolysis with alcoholic potash, the ethereal salt is decomposed into dimethyldiacetylpentane, dimethylacetylcaproic acid and dimethylpimelic acid, the relative quantity of each of these three compounds depending to a considerable extent on the concentration of the alcoholic potash and on the manner in which the hydrolysis is carried out.

αα′-Dimethyl-αα′-diacetylpentane, $CHMeAc\cdot[CH_2]_3\cdot CHMeAc$, is a colourless oil boiling at 198—201° under a pressure of 112 mm.: it shows no signs of crystallising even when cooled to 0°. The *dihydroxime*, $OH\cdot N{:}CMe\cdot CHMe\cdot[CH_2]_3\cdot CHMe\cdot CMe{:}N\cdot OH$, crystallises from a mixture of benzene and light petroleum in colourless needles melting at 95—96°.

αα′-Dimethypimelic acid, $COOH\cdot CHMe\cdot[CH_2]_3\cdot CHMe\cdot COOH$, separates from light petroleum in compact, colourless crystals, and melts at 74—75°; it is readily soluble in water and most organic solvents. The *silver* salt, $C_9H_{14}O_4Ag_2$, is a colourless, seemingly amorphous compound, only sparingly soluble in boiling water.

Ethylic dimethylpimelate, $C_9H_{14}O_4Et_2$, is formed in large quantities when ethylic methylacetoacetate is treated with sodium ethoxide and trimethylene bromide in alcoholic solution in presence of a small quantity of water; under these conditions the ethylic dimethyldiacetylpimelate which is produced in the first case seems to be completely converted into the ethylic dimethylpimelate. It is a colourless oil boiling at 190—191°. On hydrolysis with alcoholic potash it is converted into dimethylpimelic acid.

αω-Dimethyl-ω-acetylcaproic acid, $CHMeAc\cdot[CH_2]_3\cdot CHMe\cdot COOH$, is a thick, colourless oil boiling at about 218—220° under a pressure of 60 mm.; it cannot easily be obtained in a pure condition.

58. "Berberine." Part II. By W. H. Perkin, jun., Ph.D., F.R.S.

In Part I of this research (*cf. Chem. Soc. Trans.*, 1889, 63) the results of preliminary experiments on the oxidation of berberine with

varying quantities of potassium permanganate were briefly described, and a short account of some new substances obtained during these experiments was appended. In the further prosecution of this research very large quantities of the alkaloid have been oxidised. The amounts used in the experiments varied considerably, but some of the best results were obtained where, in each operation, 7 grams of berberine, 9 grams of potassium permanganate and about 1 gram of potassium carbonate were used. The product from a number of such operations was treated with sulphur dioxide until the whole of the manganese precipitate had been brought into solution; the resulting yellow precipitate was then separated from the yellow solution (A) by filtration, washed with water, and warmed to 40° with a dilute sodium carbonate solution, by which means about one-half of the precipitate was dissolved (B).

The insoluble residue contains, besides two substances—berberilic anhydride, $C_{20}H_{17}NO_8$ (m. p. 236—237°), and berberal, $C_{20}H_{17}NO_7$ (m. p. 150°)—which have been already described, a new base, $C_{20}H_{19}NO_9$, which is very sparingly soluble in water, and crystallises in flat, yellow plates; and small quantities of two other substances.

The alkaline solution (B) contains, as principal product, α-berberilic acid, $C_{20}H_{19}NO_9$, which was described in the former paper. This acid, when heated to 180°, is converted into berberilic anhydride; in other respects it shows great similarity to β-berberilic acid, which is described below.

The solution (A) was evaporated in large flat basins to about half its bulk, filtered from the precipitate (C) which separates and then evaporated to a small bulk (D). The precipitate (C) was warmed with dilute chlorhydric acid till free from inorganic matter, the residue washed with water, dried, and extracted with hot acetic acid, by which means a quantity of berberilic anhydride was removed. The insoluble residue was dried and dissolved in a small quantity of boiling aniline, from which solution it was deposited, on cooling, in glittering, yellow plates, having the composition $C_{20}H_{17}NO_6$.

This substance, which is formed in very small quantities, has only been superficially examined. It is characterised by its insolubility in the usual solvents, and by the fact that it yields a beautifully crystalline potassium salt when dissolved in alcoholic potash.

The highly concentrated liquors (D) were extracted 30 times with ether, the ether evaporated and the semi-solid residue boiled with water until the greater part had dissolved (E). The residue dissolved almost entirely in dilute sodium carbonate solution (P), leaving a dark brown pasty residue, from which, by treatment with glacial acetic acid, a substance crystallising in long, brown needles can be isolated. This substance melts at 167°, has the formula $C_{10}H_8O_5$, and

dissolves in alkali with formation of an acid, which crystallises from water in long, glittering needles, m. p. 147°.

The alkaline solution (F), acidified with chlorhydric acid, deposits a brown, amorphous precipitate, which crystallises from glacial acetic acid in glittering, colourless plates which melt at 200° with decomposition and charring.

This substance, which has the composition $C_{20}H_{15}NO_7$, is a monobasic acid, yielding highly characteristic salts, of which the silver salt, $C_{20}H_{14}NO_7Ag$, was analysed. The calcium, lead and zinc salts are sparingly soluble, but beautifully crystalline.

The solution (F) was next examined. This was heated to boiling, rendered slightly alkaline with sodium carbonate and allowed to stand 24 hours. At the end of this time the liquid is found to be filled with a mass of glittering plates of a new base, $C_{10}H_9NO_3$, which will be described in detail later on. These are filtered off, the alkaline solution neutralised with chlorhydric acid, and mixed with an excess of a strong solution of calcium chloride. No precipitate is produced in the cold, but on boiling, a crystalline calcium salt separates. This is collected, washed with a little water, dissolved in hot dilute hydrochloric acid, from which solution, on standing, a quantity of crystals separate. These crystals are a mixture of two acids, which both melt at 180°, and which can be separated by recrystallisation from water. The more soluble acid is hemipinic acid. The second acid crystallises from water, without water of crystallisation, in colourless plates, which, on analysis, give numbers agreeing with the formula $C_6H_6O_6$. The silver salt has the composition $C_9H_4O_6Ag_2$. This acid is most probably identical with hydrastic acid,

$$CH_2<^{O}_{O}>C_6H_2(COOH)_2,$$

which Freund and Lachmann (*Berichte*, **22**, 2324) obtained from hydrastinine, and which melts at 175°.

The following are the results of the examination of the principal products described above.

1. *Berberilic anhydride* ($C_{20}H_{17}NO_8$, m. p. 236—237°), does not combine with phenylhydrazine. When boiled with acetic anhydride for some hours it is converted into an acetate, $C_{20}H_{16}NO_7(C_2H_3O_2)$, which crystallises from acetic anhydride in hard, light-yellow prisms melting at 140°. Boiling dilute sulphuric acid decomposes this acetate quantitatively into berberilic anhydride and acetic acid. Pentachloride of phosphorus converts berberilic anhydride into a chloride, $C_{20}H_{16}NClO_7$, which crystallises from benzene in hard, garnet-red prisms melting at 167°. This substance is readily acted on by water and reconverted into berberilic anhydride. Berberilic anhydride dissolves readily in

warm dilute caustic soda solution, with formation of β-berberilic acid, which is precipitated on the addition of acids as a white, sticky mass, which becomes hard on standing.

This new acid crystallises from dilute alcohol in warty masses, and melts at 180°, being at this temperature reconverted into its anhydride. Its composition is $C_{20}H_{19}NO_9$, and it is isomeric with α-berberilic acid, which melts at about 140°.

A number of salts were prepared by precipitating a neutral solution of the ammonium salt with various agents. These salts, however, are not derived from berberilic acid, $C_{20}H_{19}NO_9$, but all contain one molecule of water less, and are therefore derivatives of the anhydride $C_{20}H_{17}NO_8$. The silver salt, $C_{20}H_{16}AgNO_8$, is a white, amorphous mass. The methylic salt, $C_{20}H_{16}(CH_3)NO_8$, prepared by the action of methyl iodide on the silver salt, crystallises from acetic acid in glittering plates which melt at 178—179°. As it was thought possible that the methyl-group might be attached to nitrogen, the action of hydrogen iodide on this methyl salt was investigated, and it was found that three methoxy-groups were present, two belonging to the berberine molecule. The substance is therefore a true methylic salt.

The most important reaction of β-berberilic acid is the change which this substance undergoes on hydrolysis. When boiled with dilute sulphuric acid (5 per cent.), it dissolves completely, being converted quantitatively into hemipinic acid and a new base: $C_{20}H_{19}NO_9 + H_2O = C_{10}H_{10}O_6 + C_{10}H_{11}NO_4$, small quantities of berberilic anhydride being always regenerated during the decomposition.

After extracting the hemipinic acid by ether, the sulphuric acid liquors are evaporated to a small bulk, and then allowed to stand 48 hours, when the sulphate of the base separates in large, slightly brownish coloured tablets. These are collected, dissolved in water, treated by the calculated quantity of baryta-water, and the solution gently evaporated. The concentrated solution deposits the base in large, flat, monoclinic plates which melt at 180—182°, and contain 1 mol. of water. The platinochloride, $(C_{10}H_{11}NO_4HCl)_2PtCl_4$, crystallises from water in dark-yellow needles which melt at about 220°. Nitrous acid converts the base into a substance of the formula $C_{10}H_8O_4$, which will be described later on.

When heated to 180°, or digested with strong potash solution, or even simply boiled with water for some time, the base loses the elements of a molecule of water, and is converted into another base, $C_{10}H_9NO_3$.

This important substance crystallises from water in magnificent colourless, glittering plates which melt at 182°. It is feebly basic, its salts being only stable in the presence of large quantities of acid.

It is a very stable substance, and when boiled with dilute nitric acid is principally converted into a nitro-derivative, $C_{10}H_8(NO_2)NO_3$, which crystallises from water in yellow plates, m. p. 175—180°. If the base be dissolved in a large quantity of dilute chlorhydric acid (1HCl to $2H_2O$), well cooled, and the calculated quantity of sodium nitrite (1 mol. prop.) added, an immediate precipitate of a yellow nitroso-compound, $C_{10}H_8(NO)NO_3$, is produced. This crystallises from alcohol in glittering, yellow needles which melt at 195—196° with decomposition. When boiled with dilute caustic soda, this nitroso-compound rapidly dissolves with evolution of nitrogen, $C_{10}H_8(NO)NO_3 + H_2O = C_{10}H_{10}O_5 + N_2$.

The new substance melts at 146°, and is readily soluble in hot water and most of the usual solvents. It is an acid, the salts of which are fairly characteristic. The silver salt, $C_{10}H_9AgO_5$, is crystalline, and soluble in hot water. When heated to 150°, or boiled with water, this substance readily loses 1 mol. of water, and is converted into its anhydride, $C_{10}H_8O_4$.

This substance crystallises from water in large, flat plates which melt at 126° and distils almost without decomposition. It is reconverted by dissolution in alkalis into the acid $C_{10}H_{10}O_5$. Nitric acid produces a light-yellow mononitro-compound, $C_{10}H_7(NO_2)O_4$, which melts at 197°. A number of experiments were tried with the object of oxidising the molecule to some well-known acid, but without success, the substance being either unacted on or else completely destroyed by the oxidising agents employed. Gently fused with potash, the substance yields a mixture of pyrocatechol and protocatechuic acid.

When heated with hydriodic acid in Zeisel's apparatus, no trace of methyl iodide was evolved, a proof that the molecule contains no methoxyl-groups; chlorhydric acid (1HCl to $4H_2O$) at 170—175° decomposes the substance, however, and apparently quantitatively, with deposition of carbon and formation of a new compound, $C_9H_8O_4 = C_{10}H_8O_4 - C$.

This compound crystallises from water, in which it is very soluble, in warty masses which melt at about 220—225°. Its aqueous solution shows with ferric chloride the most intense pyrocatechol reaction; it gives a white precipitate with acetate of lead, and reduces both Fehling's solution and ammoniacal nitrate of silver.

The result shows that all these derivatives contain the piperonyl-group, $CH_2{<}^{O}_{O}{>}C_6H_4$, the constitution and proposed nomenclature of these substances being apparent from the following table:—

$C_{10}H_{11}NO_4 = CH_2<^{O}_{O}>C_6H_2<^{COOH}_{CH_2\cdot CH_2\cdot NH_2}$ = ω-Amidoethylpiperonylcarboxylic acid.

$C_{10}H_9NO_3 = CH_2<^{O}_{O}>C_6H_2<^{CO-NH}_{CH_2-CH_2}$ = ω-Amidoethylpiperonylcarboxylic anhydride.

$C_{10}H_{10}O_5 = CH_2<^{O}_{O}>C_6H_2<^{COOH}_{CH_2\cdot CH_2\cdot OH}$ = ω-Hydroxyethylpiperonylcarboxylic acid.

$C_{10}H_8O_4 = CH_2<^{O}_{O}>C_6H_2<^{CO-O}_{CH_2\cdot CH_2}$ = ω-Hydroxyethylpiperonylcarboxylic anhydride.

$C_9H_8O_4 = {}^{HO}_{HO}>C_6H_2<^{CO-O}_{CH_2\cdot CH_2}$ = ω-Hydroxyethylpyrocatecholcarboxylic anhydride.

Freund and Will (*Berichte*, **20**, 2400), in their researches on hydrastine, describe a substance, oxyhydrastinine, obtained by the action of caustic potash on hydrastinine, which they subsequently prove to have the constitution $CH_2<^{O}_{O}>C_6H_2<^{CO-N\cdot CH_3}_{CH_2-CH_2}$.

If the formulæ assigned to the compounds above be correct, this oxyhydrastinine must be a methyl-derivative of the compound $C_{10}H_9NO_3$, and in order to confirm these formulæ every effort was made to convert the substance $C_{10}H_9NO_3$ into oxyhydrastinine.

The experiments first made in this direction are the following:—

1. $C_{10}H_9NO_3$ and $C_{10}H_{11}NO_4$ were treated with methyl iodide under various conditions, with and without the addition of alkali.

2. $C_{10}H_8O_4$ was heated with methylamine and with methylamine acetate in a sealed tube.

3. $C_{10}H_{10}O_5$ was converted into the methylamine salt, and this was distilled.

But all these experiments failed to produce the change desired. The transformation was, however, ultimately accomplished in the following way:—The compound $C_{10}H_8O_4$ is converted by phosphorus pentachloride into the chloride $C_{10}H_9O_4Cl$, which crystallises from chloroform in glittering needles melting at 159°. This substance is remarkable for the ease with which it loses hydrogen chloride, and is reconverted into $C_{10}H_8O_4$. This change takes place on heating to 150°, or on heating with alkalis, or reducing with zinc-dust and acetic acid, and also on heating with methylamine in alcoholic solution in a sealed tube.

In order to prevent this, the carboxyl-group was protected by converting the chloride into its methylic salt. For this purpose,

$C_{10}H_8O_4$ was treated in chloroform solution with an excess of pentachloride of phosphorous, the chloroform distilled off, and the residue poured into methyl alcohol. The methylic salt was thus obtained as a white powder, which crystallised from dilute methyl alcohol in beautiful woolly tufts of needles melting at 83°.

When this was heated with methylamine in alcoholic solution at 130° for six hours and the product was boiled with alcoholic potash, oxyhydrastinine was almost quantitatively obtained, thus :—

$$CH_2<^{O}_{O}>C_6H_2<^{COOCH_3}_{CH_2\cdot CH_2Cl} + NH_2CH_3 =$$

$$HCl + CH_2<^{O}_{O}>C_6H_2<^{COOCH_3}_{CH_2\cdot CH_2\cdot NHCH_3} =$$

$$CH_2<^{O}_{O}>C_6H_2<^{CO\cdot NCH_3}_{CH_2\cdot CH} + CH_3OH.$$

The substance obtained in this way melted at 98°, and showed all the properties of oxyhydrastinine.

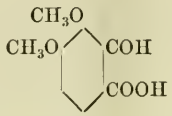
2. *Berberal*, $C_{20}H_{17}NO_7$; m. p. 150°.—When in a finely-divided state and very pure, berberal is moderately readily hydrolysed by boiling dilute sulphuric acid (containing 20 per cent. H_2SO_4), a clear, slightly brownish-coloured solution resulting. Ether extracts from this solution a colourless crystalline mass which, when treated with dilute sodium carbonate, is separated into the base $C_{10}H_9NO_3$, described above, and a new acid. This latter substance crystallises from water in beautiful long, satiny needles which melt at 121°, and on analysis give numbers agreeing with the formula $C_{10}H_{10}O_8$. The analysis of the silver salt, $C_{10}H_9AgO_5$, showed the acid to be monobasic. When treated with hydrogen iodide in Zeisel's apparatus, results were obtained which proved that the acid contained two methoxyl-groups. Fusion with potash converts the acid into protocatechuic acid; but if caustic potash solution (sp. gr. 1·4) be employed and the acid simply digested with this on a reflux apparatus, an almost quantitative yield of veratric acid, $(CH_3O)_2C_6H_3COOH$ (m. p. 177—178°), is obtained.

When subjected to the action of hydroxylamine in alkaline solution at ordinary temperatures, a hydroxime, $C_{10}H_{11}NO_5$, is produced. This crystallises in fine needles which, when heated, melt at 124°, but at once become solid again, and then do not again melt till the temperature is raised to 213°. In order to investigate this decomposition, the pure hydroxime was heated to 180° for 15 minutes and the residue recrystallised from alcohol. Beautiful needles were thus obtained which melted at 224—226°, and were readily identified as hemipinimide.

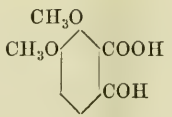
The acid $C_{10}H_{10}O_5$ is readily reduced by sodium amalgam, being

converted into an acid which, when precipitated from its alkaline solution by the addition of an acid, at once loses water with formation of pseudomekonin, $\begin{matrix}CH_3O\\CH_3O\end{matrix}>C_6H_2<\begin{matrix}CH_2\\CO\end{matrix}>O$.

This substance crystallised from water in long needles melting at 122—123°, and possessed all the properties ascribed to pseudomekonin by Solomon (*Ber.*, **20**, 884). These experiments prove conclusively that the acid $C_{10}H_{10}O_5$ has the constitution represented by the formula



and it thus bears a very close relationship to opianic acid,



which is brought out in a most interesting way by a parallel study of the reactions of the two substances; thus, for instance, on reduction both yield mekonins, and with hydroxylamine both yield hydroxymes, which, when gently warmed, are converted into hemipinimide. The acid $C_{10}H_{10}O_5$ may therefore be called *pseudopianic acid.*

These experiments throw considerable light on the constitution o *berberal.* This substance on hydrolysis yields pseudopianic acid and the base $CH_2<\begin{matrix}O\\O\end{matrix}>C_6H_2<\begin{matrix}CO-NH\\CH_2-CH_2\end{matrix}$; its constitution is therefore probably represented by the formula

$$\begin{matrix}CH_3\cdot O\\CH_3\cdot O\end{matrix}>C_6H_2<\begin{matrix}CO\cdot C(OH)-\\CO\cdot N\cdot CH_2\cdot CH_2\end{matrix}>C_6H_2<\begin{matrix}O\\O\end{matrix}>CH_2.$$

Berberilic anhydride, $C_{20}H_{17}NO_8$, yields on hydrolysis hemipinic acid and the base

$$CH_2<\begin{matrix}O\\O\end{matrix}>C_6H_2<\begin{matrix}COOH\\CH_2\cdot CH_2\cdot NH_2\end{matrix};$$

it has, therefore, possibly the following constitution :—

$$\begin{matrix}CH_3O\\CH_3O\end{matrix}>C_6H_2<\begin{matrix}CO\cdot O\cdot CO\text{———}\\CO\cdot NH\cdot CH_2\cdot CH_2\end{matrix}>C_6H_2<\begin{matrix}O\\O\end{matrix}>CH_2.$$

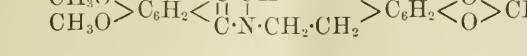
These experiments also show :—

1. The nature of all the oxygen-atoms in the molecule of berberine, $C_{20}H_{17}NO_4$, thus precluding the hypothesis that berberine owes its colour and tinctorial power to the presence of a quinone-group.

2. That berberine is an isoquinoline-derivative.

3. That berberine is closely related to hydrastine, narcotine and papaverine.

Further experiments must decide the question of the exact constitution of berberine; but the author is of the opinion that the following formula explains well all the reactions of this alkaloid which have hitherto been investigated.



The discussion of this formula will be attempted in the detailed paper.

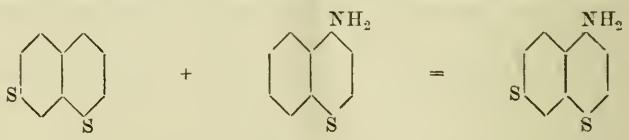
59. "Studies on the constitution of the tri-derivatives of naphthalene. No. 4. The constitution of α-naphthylaminedisulphonic acid Dahl No. II. Naphthalene-1 : 2'-disulphonic acid." By Henry E. Armstrong and W. P. Wynne.

When naphthionic acid is sulphonated with 35 per cent. anhydrosulphuric acid at a temperature not exceeding 30° according to Dahl and Co.'s German patent No. 41957, 1886, two disulphonic acids are produced, which are respectively known as α-naphthylaminedisulphonic acid No. II and No. III, the latter constituting the chief product. The constitution of acid No. III has been given in a previous communication (these Proceedings, 1890, 16). With the object of comparing the disulphonic acids obtained by the sulphonation of α-naphthylamine with those known to be produced by the sulphonation of α-naphthol, the authors have undertaken the investigation of acids Nos. I and II of Dahl and Co.'s patent, and are now in a position to communicate the results obtained by the examination of acid No. II, for a liberal supply of which they are indebted to Messrs. Dahl and Co.

The product received was in the form of potassium salt, and appeared to be uniform; but on investigation it was found to contain a noteworthy quantity, perhaps 20 per cent., of an α-naphthylaminetrisulphonic acid, the formation of which, under the conditions above named, is specially interesting as throwing further light on the process involved in the production of isomeric disulphonic acids. When reduced by the hydrazine method, this α-naphthylaminetrisulphonic acid yields a *naphthalenetrisulphonic acid* characterised by forming a *chloride*, $C_{10}H_5(SO_2Cl)_3$, which crystallises from a mixture of benzene and petroleum spirit in small prisms melting at about 191°; whilst by the Sandmeyer method it is converted into a *chloronaphthalenetrisulphonic acid* characterised by forming a chloride,

$C_{10}H_4Cl(SO_2Cl)_3$, which crystallises from benzene in minute prisms from a mixture of benzene and petroleum spirit in small crystalline aggregates, and from acetic acid in small scales melting at 215°.

α-Naphthylaminedisulphonic acid No. II, on conversion into naphthalenedisulphonic acid by v. Baeyer's hydrazine method, yields a new acid, the salts of which will be described in a subsequent communication. The *chloride* of this acid, $C_{10}H_6(SO_2Cl)_2$, crystallises from benzene, in which it is readily soluble, in prismatic forms; from a mixture of benzene and petroleum spirit in tufts of opaque irregular needles; and from acetic acid in beautiful glistening plates; it melts at 122·5°, and on distillation with PCl_5 yields a dichloronaphthalene melting at 63—63·5°, convertible by sulphonation, &c., into a sulphochloride, crystallising in needles, which become opaque and melt at 117°. The acid is consequently the 1 : 2′-disulphonic acid, and is the *sixth* known naphthalenedisulphonic acid. By the Sandmeyer method, acid No. II can be converted into a chlorodisulphonic acid the *chloride* of which crystallises from a mixture of petroleum spirit and benzene in minute needles, and from acetic acid in small prisms; it melts at 126—127°, and, on distillation with PCl_5, yields 1 : 4 : 3′-trichloronaphthalene, characterised, among other properties, by melting both at 56° and 66° under the conditions already described (*loc. cit.*). Superposing these results, it follows that α-naphthylaminedisulphonic acid Dahl No. II is, as its mode of formation would seem to indicate, a sulphonated naphthionic acid, and that it has the constitution :—



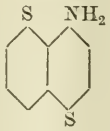
Dahl acid No. II.

The authors reserve the investigation of the properties of the 1 : 2′-naphthalenedisulphonic acid and its derivatives.

60. "Studies on the constitution of the tri-derivatives of naphthalene. No. 5. The constitution of the Schöllkopf α-naphthylaminedisulphonic acid." By Henry E. Armstrong and W. P. Wynne.

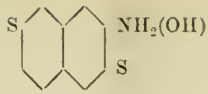
The formation of the Schöllkopf α-naphthylaminedisulphonic acid (German patent 40571) by the nitration and subsequent reduction of the authors' naphthalene-1 : 4′-disulphonic acid (Bernthsen, *Ber.*, 1889 3327) renders it evident that the generally accepted view of the constitution of this acid is a correct one. Having been favoured by the Actiengesellschaft für Anilinfabrikation with a supply of the material prepared by the method given in the Schöllkopf patent, the authors took occasion to submit this to examination. They find

that it is converted by the hydrazine method into naphthalene-1 : 4′-disulphonic acid, which was characterised by conversion into the chloride crystallising from benzene in prisms melting at 182°, and into 1 : 4′-dichloronaphthalene melting at 107°. On treatment by the Sandmeyer process it gave a chlorodisulphonic acid, the *chloride* of which crystallised from acetic acid in very small, prismatic needles which became opaque on drying, and from a mixture of petroleum spirit and benzene in sparingly soluble glistening flat plates; it melted at 135°, and, on distillation with PCl_5, was converted into ĉ- or 1 : 4 : 1′-trichloronaphthalene melting at 131°. These results place it beyond question that the constitution of the Schöllkopf acid is expressed by the formula



61. "Studies on the constitution of the tri-derivatives of naphthalene. No. 6. The constitution of Cassella's β-naphthylamine-ĉ-disulphonic acid." By Henry E. Armstrong and W. P. Wynne.

Messrs. Cassella and Co. having been good enough to furnish the authors with a supply of their β-naphthylamine-ĉ-disulphonic acid, prepared from the β-naphtholdisulphonic acid of their German patent No. 44079, it has been possible to determine its constitution by the hydrazine and Sandmeyer methods already described. On treatment by the hydrazine method, the amido-acid yields, in the first instance, a peculiar ropy, gelatinous hydrazine, which can only be freed from tin salts with considerable difficulty. The disulphonic acid obtained from this hydrazine yields a chloride crystallising from benzene, in which it is sparingly soluble, in small, flat, spear-like needles; this chloride melts at 225°, and on distillation with PCl_5 yields 2 : 3′-dichloronaphthalene melting at 135°: it is, therefore, naphthalene-2 : 3′-disulphonic acid—the β-disulphonic acid of Ebert and Merz. By the Sandmeyer method, the amido-acid is converted into a chlorodisulphonic acid, the *chloride* of which crystallises from benzene, in which it is very soluble, in small, characteristic radiate groups of very slender needles, and from a mixture of petroleum spirit and benzene in small, opaque aggregates melting at 176°; on distillation with PCl_5 it yields 2 : 3 : 2′-trichloronaphthalene melting at 90°. Combining these results, it follows that Cassella's β-naphthylamine-ĉ-disulphonic acid and the β-naphtholdisulphonic acid of the German patent No. 44097, from which it is derived, have the formula



and both are, therefore, tri-β-acids isomeric with the corresponding R-acids (these Proceedings, 1890, 12).

62. "Studies on the constitution of the tri-derivatives of naphthalene. No. 7. The disulphonic acids obtained by sulphonating the isomeric heteronucleal β-naphthylaminesulphonic acids." (First notice.) By Henry E. Armstrong and W. P. Wynne.

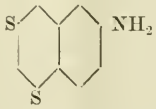
According to Gans and Co's German patent, No. 35019, 1884, β-naphthylamine is converted into the amido-G-disulphonic acid by heating its sulphate with thrice its weight of 20—30 per cent. anhydrosulphuric acid at 110—140° until soluble in water; and the same product is said to result when "β-naphthylaminesulphonic acid" is similarly treated. But inasmuch as four monosulphonic acids are obtainable from β-naphthylamine, to determine the law of sulphonation, it was obviously necessary to examine the behaviour of each of these and to avoid the occurrence of secondary changes as far as possible; experiments with this object in view were commenced several years ago: meanwhile an account of the behaviour of the Brönner acid under conditions similar to those specified by Gans and Co., have been published by Forsling (*Berichte*, 1888. 3496).

(1.) 2 : 1′-*β-Naphthylamine-α-sulphonic Acid* (*Badische acid*) :—When the Badische acid is stirred into four times its weight of 20 per cent. anhydrosulphuric acid at a temperature not exceeding 20°, and the mixture is allowed to stand, sulphonation proceeds slowly and is not entirely complete even at the end of three months. The product is found to consist almost entirely of an acid recognised as amido-G-disulphonic acid, inasmuch as it gave by the hydrazine and Sandmeyer methods all the products already described as characteristic of this acid (these Proc., 1890, 12). The naphthalenedisulphochloride prepared from it melted at 137°, and on distillation with PCl_5 gave 1 : 3-dichloronaphthalene melting at 61·5°; the chloronaphthalenedisulphochloride from it melted at 169°, and on distillation with PCl_5 gave 1 : 3 : 2′-trichloronaphthalene melting at 113°. The subsidiary product formed on sulphonating the Badische acid has not yet been prepared in sufficient quantity to admit of its examination.

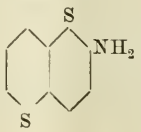
(2.) 2 : 4′-*β-Naphthylamine-α-sulphonic Acid* (*Dahl acid*).—When stirred into four times its weight of 20 per cent. anhydrosulphuric acid at a temperature not exceeding 20°, the Dahl acid gradually

undergoes further sulphonation, the process being usually completed in from 116—120 hours. The product is found to consist of two isomeric acids, which are readily separated by crystallising out the minor product as normal potassium salt, and subsequently purifying the chief product by repeated crystallisation of its acid potassium salt.

Chief Product.—The acid potassium salt of the chief product crystallises in thistle-down like aggregates, and is very soluble in water; on reduction by the hydrazine method it gave naphthalene-1 : 3-disulphonic acid which was characterised by means of the chloride melting at 137°; on distillation with PCl_5, this gave 1 : 3-dichloronaphthalene melting at 61·5° (*loc. cit.*). On treatment by the Sandmeyer process, it was converted into a chlorodisulphonic acid, the *chloride* of which is very soluble in benzene, and crystallised from a mixture of benzene and petroleum spirit in radiate groups of small prisms, from acetic acid in elongated prismatic needles showing good end-faces; this chloride melted at 156°, and on distillation with PCl_5 gave 2 : 2′ : 4′-trichloronaphthalene crystallising in radiate groups of very slender, characteristic needles melting at 80°. It follows, therefore, that the chief product obtained by the further sulphonation of the Dahl acid under the conditions named has the constitution

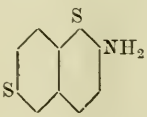


Minor Product.—The normal potassium salt of this acid was obtained in well-formed rectangular tablets. The quantity prepared has not sufficed for its complete investigation by both methods, and it has therefore been examined by the Sandmeyer method alone. The corresponding chlorodisulphonic acid yields a *chloride* which crystallises from benzene, in which it is sparingly soluble in the cold, either in prismatic needles or well-formed prisms, from a mixture of benzene and petroleum spirit in flat needles and from acetic acid in long, prismatic, flat needles; it melts at 158°, and on distillation with PCl_5 is converted into 1 : 2 : 4′-trichloronaphthalene, crystallising from alcohol in long, slender, flat needles melting at 78—78·5° (these Proc., 1889, 49). It follows, therefore, that this amido-acid has the constitution



(3.) 2 : 3′-*β*-*Naphthylamine*-*β*-*sulphonic Acid* (*Brönner acid*).—When stirred into four times its weight of 20 per cent. anhydrosulphuric acid at a temperature not exceeding 20°, the Brönner acid is readily further sulphonated, the process being completed in from 16—20 hours. The product is found to consist of two isomeric acids; the minor product, perhaps 20 per cent., has been identified as G-amido-disulphonic acid by the hydrazine and Sandmeyer methods (*v. supra*).

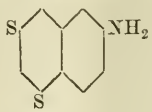
Chief Product.—The acid potassium salt of this acid crystallises in opaque, white radiate aggregates of short needles, difficultly soluble in water; but the crystalline form and solubility are much influenced by the presence of small quantities of amido-G-acid, and there is every reason to regard it as identical with the acid obtained by Forsling (*Ber.*, 1888, 3496) by heating Brönner acid with 3 to 4 parts of "fuming sulphuric acid" (percentage of added SO_3 not stated) at 110° until the product was soluble in water. When reduced by the hydrazine process, the amido-acid constituting the chief product gave naphthalene-1 : 3′-disulphonic acid, which was characterised by means of its sulphochloride melting at 127°, and the derived 1 : 3′-dichloronaphthalene melting at 48·5°. On treatment by the Sandmeyer process, it was converted into a chlorodisulphonic acid, the *chloride* of which crystallised from benzene, in which it was readily soluble, in well-formed prisms, from a mixture of benzene and light petroleum in small prisms showing good faces, and from acetic acid in prismatic needles; it melted at 124·5—125°, and on distillation with PCl_5 gave 1 : 2 : 3′-trichloronaphthalene crystallising from alcohol in tufts of short, very slender needles melting at 92° (these Proc., 1889, 52). Combining these results, the amido-acid constituting the chief product, and presumably Forsling's acid, has the constitution:—



By operating at higher temperatures the yield of this acid is diminished, and that of the amido-G-acid increased.

(4.) 2 : 2′-*β*-*Naphthylamine*-*β*-*sulphonic Acid* (Bayer and Duisberg's delta-acid).—When stirred into four times its weight of 20 per cent. anhydrosulphuric acid at a temperature not exceeding 25°, delta-acid yields a complex product, which has not yet been satisfactorily separated into its constituents. Although the acid was very carefully purified and, it is believed, was freed from Brönner acid, one of the disulphonic acids obtained from it and forming a considerable proportion of the product, had the constitution and properties of the *β*-naphthylamine-1 : 3′-disulphonic acid prepared from pure Brönner

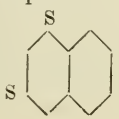
acid. Two other products were obtained and are at present under investigation; one of these is converted by the Sandmeyer process into a chlorodisulphonic acid which seems to be identical with that derived from the sulphonated Dahl acid of the constitution



The investigation of the changes which occur in the conversion of these various acids into amido-R-acid on the one hand and the Cassella β-naphthylamine-δ-disulphonic acid on the other are at present under investigation, and the authors hope to be in a position shortly to communicate in a final form results indicating the influence exercised by NH_2, as compared with Cl and OH in a β-position on the formation of disulphonic acids.

63. "Studies on the constitution of the tri-derivatives of naphthalene. No. 8. β-Chloronaphthalenedisulphonic acids." (First notice.) By Henry E. Armstrong and W. P. Wynne.

As already indicated in a previous communication, the study of the disulphonic acids obtained by sulphonating chloronaphthalenesulphonic acids of known constitution is being carried on *pari passu* with that of the acids derived from the various naphthylaminesulphonic acids (these Proc., 1890, 18). A brief account of the results obtained with the four heteronucleal β-chloronaphthalenesulphonic acids under like conditions is now given, details with reference to the composition of the salts, &c., being reserved for a full communication. Sulphonation was effected by adding the theoretical quantity of sulphuric anhydride, employed in the form of 20 per cent. anhydrosulphuric acid, to the dry potassium β-chloronaphthalenesulphonate and heating the warm mixture at 100° for an hour, the potassium sulphate formed being removed by treatment with alcohol and the excess of sulphuric acid by means of barium carbonate.

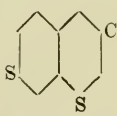
(1.) 2 : 1'-*β-Chloronaphthalene-α-sulphonic Acid.*—This acid, under the conditions named, gives a uniform chloronaphthalenedisulphonic acid, the *chloride*, $C_{10}H_5Cl(SO_2Cl)_2$, of which crystallises from benzene, in which it is comparatively sparingly soluble, in beautiful radiate groups of long, slender, lustrous needles; it melts at 170°, and on distillation with PCl_5 gives 1 : 3 : 2'-trichloronaphthalene melting at 113°. The constitution of the acid is therefore  , and cor-

responds with the G-amido-acid obtainable from the 2 : 1′-β-naphthylamine-α-sulphonic acid.

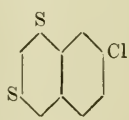
(2.) 2 : 4′-*β-Chloronaphthalene-α-sulphonic Acid.*—This acid gives what seems to be a uniform product. The potassium salt of the chlorodisulphonic acid is particularly well characterised, since it crystallises in prismatic forms, whereas the corresponding salts of the isomeric acids crystallise in slender needles. The *chloride*, $C_{10}H_5Cl(SO_2Cl)_2$, is apparently dimorphous and crystallises from benzene for the most part in very lustrous scales, but occasionally in prismatic forms, both of which melt at 156—156·5°, and on distillation with PCl_5 give the same trichloronaphthalene melting at 79°. This trichloronaphthalene has not yet been compared by sulphonation, &c., with the 1 : 2 : 4′- and the 1 : 3 : 3′-trichloronaphthalenes, with one of which it must be identical, owing to the insufficient supply of material; most probably it has the constitution 1 : 3 : 3′- and corresponds with that derived from the amido-acid constituting the chief product of the further sulphonation of the 2 : 4′-β-naphthylamine-α-sulphonic acid.

(3.) 2 : 3′-*β-Chloronaphthalene-β-sulphonic acid.*—Under the conditions named, this acid gives two chlorodisulphonic acids which are best separated by the fractional crystallisation of the potassium salts. The less soluble potassium salt constituting the minor product yields a *chloride* $C_{10}H_5Cl(SO_2Cl)_2$, which crystallises from benzene in aggregates of what at first sight seemed to be radiate prisms, but under a lens were found to be composed of bundles of very slender needles aggregated in prismatic forms, having a silky lustre; it melts at 148°, and on distillation with PCl_5 gives 1 : 3 : 2′-trichloronaphthalene, crystallising from alcohol in characteristic tufts of needles melting at 113°.

The more soluble potassium salt constituting the major product was found to give products identical with those obtained from the chlorodisulphonic acid derived from 2 : 1′-β-chloronaphthalene-α-sulphonic acid (*v. supra*). The *chloride* crystallises from benzene in radiate groups of needles melting at 169°, and on distillation with PCl_5 yields 1 : 3 : 2′-trichloronaphthalene melting at 113°. The constitution of the two acids is represented by the formulæ—



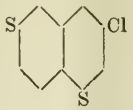
Minor product.
$Cl(SO_2Cl)_2$, m. p. = 148°.



Major product.
$Cl(SO_2Cl)_2$, m. p. = 169°.

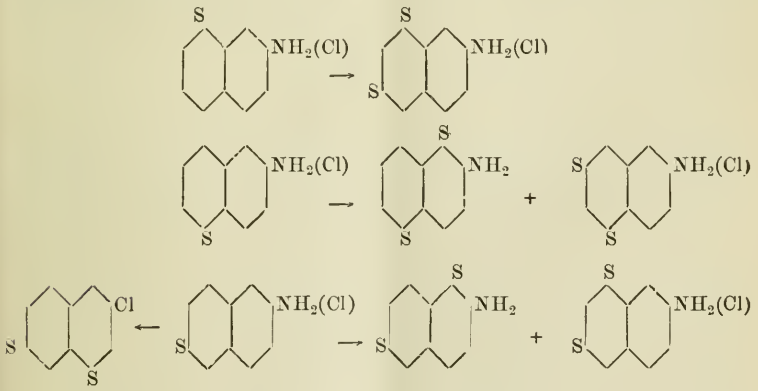
(4.) 2 : 2′-*β-Chloronaphthalene-β-sulphonic Acid.*—This acid, under

the above conditions, yields a uniform chlorodisulphonic acid, the *chloride* of which, $C_{10}H_5Cl(SO_2Cl)_2$, crystallises in beautiful radiate groups of flat, prismatic needles melting at 174°. On distillation with PCl_5 the chloride is converted into 1 : 3 : 3′-trichloronaphthalene, crystallising from alcohol in radiate groups of long, slender needles melting at 80·5°. The acid has, therefore, the constitution—



64. "The comparative influence exercised by the radicles Cl, OH and NH_2 in naphthalene-derivatives on the formation of disulphonic acids." By Henry E. Armstrong and W. P. Wynne.

The results obtained by the comparative study of the influence exercised by radicles such as Cl, OH and NH_2 on the formation of disulphonic acids, of which an account has been given in the foregoing notes and in previous communications by the authors, are such as to throw much light on the laws which govern substitution in the naphthalene series and are moreover highly suggestive. The results obtained in the case of the chloro- and amido-acids are collected in the following diagram.

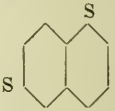


One fact to which attention may be directed, which appears to be most clearly established by the investigation of a very large number of disulphonic acids, is the "invincible objection" of two sulphonic radicles to remain in either contiguous or para- or peri-positions. The expression "remain in" is used advisedly, as the authors believe that, inasmuch as action more often than not takes place in the first instance in accordance with the so-called α-law to which they have

repeatedly directed attention, such positions are sometimes initially assumed by two sulphonic groups. It is a question whether the final acquisition of other positions than α-positions is a consequence of direct isomeric change, or of the formation of higher sulphonic acids and their subsequent partial hydrolysis.

Different radicles undoubtedly exercise a very different and most important influence in determining such secondary changes. Thus β-naphthol on treatment with sulphonating agents is converted into a sulphate which very readily undergoes isomeric change into the 2 : 3′-sulphonic acid; β-naphthylamine sulphate undergoes a similar change, but much less readily, being converted into the 2 : 3′-sulphonic acid only after long heating at a high temperature : in this latter case the formation of the *sulphamic* acid probably precedes that of the sulphonic acid, and either the sulphamic acid is formed with difficulty from the sulphate, or, when formed, does not readily undergo isomeric change.

α-Naphthylamine and α-naphthol differ in a similar manner.

When excess of sulphuric acid is used, opportunity is given for sulphonation to pursue a different course: the characteristic properties of the phenol and amine are, in a sense, obliterated owing to the formation of sulphates, and these sulphates behave much as do corresponding derivatives containing a neutral radicle-chlorine, for example. Then, if β-naphthylic sulphate be sulphonated by SO_3HCl without application of heat, a disulphonic acid is at once obtained which, there is reason to believe, has the constitution 

(*cf.* *Berichte*, 1882, 204); the formation of this compound affords the most significant indication of the course of change: evidently the *homo*-α-hydrogen atom contiguous to the $O{\cdot}SO_3H$-group of the sulphate is first displaced; the resulting sulpho-sulphate, however, spontaneously undergoes isomeric change. β-Naphthylamine sulphate, apparently, behaves somewhat differently, yielding the 2 : 1′- and 2 : 4′-monosulphonic acids: in this case the $NH_2{\cdot}H_2SO_4$-group may be supposed to remain unchanged; but it is not improbable that the homo-α-hydrogen atom contiguous to this group is primarily displaced by SO_3H, which then passes spontaneously into the contiguous peri-α-position, giving rise to the 2 : 1′-acid: the formation from the 2 : 3′- and 2 : 4′-monosulphonic acids of disulphonic acids containing the SO_3H-group in the homo-α-position contiguous to the NH_2 affords the strongest support to this view. The formation of the 2 : 4′-monosulphonic acid from β-naphthylamine sulphate is perhaps the outcome of an independent action.

In the case of β-chloronaphthalene, it is conceivable that the 2 : 1-sulphonic acid is the immediate product, and that this spontaneously changes into the 2 : 1′-acid which is actually obtained as chief product; the 2 : 3′-acid which is obtained as subsidiary product may be formed by spontaneous isomeric change from 2 : 4′-acid initially produced on sulphonation rather than by the isomeric change of the 2 : 1′-acid at the moment of formation; this view being supported by the fact that β-iodonaphthalene affords a small proportion of 2 : 4′-acid (*cf.* these Proceedings, 1889, 120).

In short, it is not impossible that the β-mono-derivatives all behave similarly on sulphonation, acting in a minor degree as naphthalene itself would, but chiefly as mono-derivatives; and that the differences in the structure of the ultimate products are due to the different manner in which secondary change takes place under the diverse influences of various β-radicles. The same argument would apply to α-compounds.

The peculiar differences manifest in the case of monosulphonic compounds are also to be noted in the case of disulphonic (*cf.* diagram, p. 133)—the product of further sulphonation is, as a rule, simpler in the case of the chloro-acid than in the case of the amido-acid; and change proceeds further in the case of the hydroxy- than in that of the NH_2-compound, as is evidenced by the formation of R- together with G-disulphohydroxy-acid under conditions which do not give rise to R-amidodisulphonic acid.

In the case of the 2 : 1′-amidosulphonic acid, the homo-α-position contiguous to the NH_2 is, perhaps, screened from attack; and either a 1 : 4-disulphonic acid is first formed, or, under the dehydrating influence of the sulphuric acid present in excess, a *sulphamic-sulphonic* acid is gradually produced, which then undergoes isomeric change: it appears not improbable, from the exceptionally slow manner in which sulphonation takes place, that the latter is the correct explanation.

The remaining three isomeric β-amidosulphonic acids, in all probability, are at an early stage—for it is possible that a sulphamic acid is the first product of sulphonation—if not initially converted into 2 : 1-homosulpho-derivatives; but it is a question whether these then undergo a simple isomeric change, or whether the final products are formed from them by their conversion into higher sulphonic acids which then suffer hydrolysis. The behaviour of 1 : 2-chloro-β-naphthylamine on sulphonation (*cf.* these Proceedings, 1889, 36, 48) appears rather to support this latter view, as the passage of the sulpho-group through the positions 1 → 2 → 3 takes place with a much greater facility than is usual in cases of non-spontaneous isomeric change. It is true that the conditions under which sulphonation is effected are

such that no water is present; but, bearing in mind the tendency of H_2SO_4 to combine with SO_3, it is by no means improbable that H_2SO_4 itself may effect the hydrolysis.

Lastly, attention may be called to the occurrence of "homo-sulphonation" in the case of the two chloro-β-sulphonic acids; the products in question are, perhaps, direct sulphonation-products, but it is also conceivable that the 2 : 1-chloro-sulphonic acid is first formed, and that this undergoes isomeric change to the 2 : 4-acid, in consequence of the guarding influence exercised by the hetero-β-sulphonic radicle.

The results obtained in the case of the Dahl No. II acid are of special interest, as one of the sulpho-groups is in the β-position alternative to that occupied in the acid which yields naphthol-yellow S; it is, hence, possible that, in the first instance, naphthionic acid yields a peri-disulphonic acid, and not the Schöllkopf acid.

The solution of these various problems will necessitate much further study; but obviously their settlement is of importance in relation to the theory of the formation of substitution-derivatives generally.

65. "Note on the action of potash on naphthalene-1 : 3-disulphonic acid." By Henry E. Armstrong and W. P. Wynne.

When the authors' naphthalenemetadisulphonic acid (these Proc., 1890, 13) is fused with 3—4 times its weight of caustic potash at 280—300° for several hours, it gives a product which consists chiefly of a *trihydroxynaphthalene*, $C_{10}H_5(OH)_3$ (C = 67·7 per cent., H = 4·6 per cent.). This crystallises from water in minute scales, from light petroleum (b. p. = 30°) in small, white aggregates of no definite form, and melts at 120—121°. It sublimes in lustrous, thin scales; is extremely soluble in ether, chloroform, carbon bisulphide, acetone and benzene; and gives no characteristic coloration with ferric chloride. The study of the action of potash on naphthalenemetadisulphonic acid is being continued.

66. "The action of zinc on dilute sulphuric acid." By F. Pullinger, B.A., B.Sc., late Scholar of Corpus Christi College, Oxford.

The author has carried out a series of experiments with zinc prepared by thrice distilling *in vacuo* zinc purchased as "chemically pure," and has arrived at the following conclusions:—

(i.) That zinc with a perfectly smooth surface is not acted on by dilute sulphuric acid which has been submitted to prolonged boiling.

(ii.) That zinc with a rough surface is readily acted on by acids, but in a less degree by those which have been boiled than by those which have not.

(iii.) That oxidising agents, such as electrolysed sulphuric acid, hydrogen peroxide and nitric acid, increase the rate of dissolution.

(iv.) That a reducing agent such as hydrogen iodide almost entirely prevents dissolution; but that those containing sulphur, such as sulphur dioxide, are without effect.

(v.) That in all probability persulphuric acid is the *vera causa* of the dissolution of zinc in the so-called "pure" sulphuric acid.

(vi.) That pure dilute sulphuric acid would, at ordinary temperatures, be entirely without action on zinc, whether the surface of the latter were rough or smooth.

67. "Acetyltrimethylenecarboxylic acid." By T. Rhymer Marshall, D.Sc., and W. H. Perkin, jun., Ph.D., F.R.S.

When ethylene bromide acts on ethylic sodacetoacetate, an oil, $C_8H_{12}O_3$, is formed which boils at 196°; on hydrolysis this yields an oily acid, $C_6H_8O_3$, to which the name Acetyltrimethylenecarboxylic acid and the formula $\begin{array}{c} CH_3\cdot CO\cdot C\cdot COOH \\ \diagup\!\diagdown \\ CH_2\text{—}CH_2 \end{array}$ were assigned (*Chem. Soc. Trans*, 1885, **47**, 834). In a research published a short time since, Lipp (*Ber.*, **22**, 1291) states, as the result of some experiments on acetopropyl alcohol, that this formula is incorrect, and must be replaced by $\begin{array}{c} CH_2{=}C\text{—}CH\cdot COOH \\ O< \quad\quad | \\ CH_2\cdot CH_2 \end{array}$.

The authors have very carefully reinvestigated the subject with the following results:—

Acetyltrimethylenecarboxylic acid and hydroxylamine readily interact forming a crystalline hydroxime, $C_6H_9NO_3$, which melts at 145°. On reduction with sodium amalgam, the acid is converted into α-ethyl-β-hydroxybutyric acid, $CH_3\cdot CH(OH)\cdot CH(C_2H_5)COOH$; this forms a thick, colourless syrup, yielding on distillation α-ethylcrotonic acid, $CH_3\cdot CH{:}C(C_2H_5)\cdot COOH$.

A drop of a solution of potassium permanganate added to a solution of acetyltrimethylenecarboxylic acid in a dilute solution of sodium carbonate is not decolorised, even on long standing—a proof that the acid is a saturated compound, and cannot have the formula ascribed to it by Lipp (compare Baeyer, *Annalen*, **245**, 146).

Acetyltrimethylenecarboxylic acid readily splits up on heating into acetyltrimethylene, $CH_3\cdot CO\cdot CH< \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}$, and carbon dioxide.

Acetyltrimethylene and hydroxylamine interact to form a hydroxime, C_5H_9NO, which crystallises from petroleum spirit in beautiful, glittering prisms. When reduced by means of sodium (in moist

ethereal solution), acetyltrimethylene yields methylpropylcarbinol, $CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$, which boils at 119·5° (compare Saytzew, Wagner, *Annalen*, **179**, 313).

Methylpropylcarbonyl acetate, $CH_3{\cdot}CH(C_2H_3O_2){\cdot}C_3H_7$, obtained by boiling the alcohol with acetic anhydride, boiled constantly at 133·5.

Dimethyldipropylglycol, $\begin{matrix}CH_3{\cdot}C(OH){\cdot}C_3H_7\\ |\\ CH_3C(OH){\cdot}C_3H_7\end{matrix}$, is produced, together with methylpropylcarbinol, by the reduction of acetyltrimethylene. It is a thick oil which boils at 220—225° (Friedel, *Jahresb.*, 1869, 513). Fuming solution of hydrogen bromide converts acetyltrimethylene, at ordinary temperatures, quantitatively into acetopropyl bromide, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br$ (b. p. 120° at 75 mm.), a proof that acetyltrimethylene cannot have the formula $\begin{matrix}CH_2{=}C-CH_2\\ O<\quad\ |\\ \quad CH_2{\cdot}CH_2\end{matrix}$.

Methyldehydropentonecarboxylic acid, $\begin{matrix}CH_3{\cdot}C{\equiv}C{\cdot}COOH\\ O<\quad\ |\\ \quad CH_2{-}CH_2\end{matrix}$, is always formed in small quantities, together with acetyltrimethylenecarboxylic acid, by the action of ethylene bromide on ethyl sodacetoacetate (Freer and Perkin, *Chem. Soc. Trans.*, 1887, **51**, 822). In one experiment, this acid was obtained in large quantities and free from acetyltrimethylenecarboxylic acid. It crystallises from benzene in large, apparently monoclinic prisms which melt at 150°. It does not interact with hydroxylamine; its alkaline solution decolorises permanganate instantly, in which respects it differs very markedly from acetyltrimethylenecarboxylic acid.

When boiled with water, methyldehydropentonecarboxylic acid is entirely converted into acetopropyl alcohol, carbon dioxide being evolved.

Methyldehydropentone, $\begin{matrix}CH_3{\cdot}C{=}CH_2\\ O<\quad\ |\\ \quad CH_2{-}CH_2\end{matrix}$, is formed when the acid is distilled. It is a colourless, ethereal liquid; b. p. 82°, rel. den. at 15° = 0·9107, magnetic rotation 5·391. When shaken with water it rapidly dissolves, forming acetopropyl alcohol.

A careful study of these results shows that acetyltrimethylenecarboxylic acid is a saturated ketonic acid, and that it cannot have the constitution proposed by Lipp. Lipp's formula represents an acid which may be identical with methyldehydropentonecarboxylic acid, but which in any case must possess properties closely allied to those observed in this acid, and which are entirely distinct from the properties of acetyltrimethylenecarboxylic acid.

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Issued 18/11/1890.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 87. Session 1890–91.

Titles of Papers received and printed in the Transactions during the recess.

68. "Crystallographical relations of the derivatives of dibenzoylcinnamene." By Alfred E. Tutton, Demonstrator in Chemistry at the Normal School of Science, South Kensington.

69. "Note on a compound from benzoin and acetone." By Francis R. Japp, F.R.S., and Julius Raschen, Ph.D.

70. "Researches on normal and mixed diazoamides." By Raphael Meldola, F.R.S., and F. W. Streatfeild, F.I.C.

71. "Note on the action of nitric acid on dibrom-α-naphthol." By Raphael Meldola, F.R.S., and Frank Hughes.

72. "A new method for the estimation of nitrates and nitrites in water." By R. Ormandy and J. B. Cohen, Ph.D., Owens College, Manchester.

73. "A new monobromocamphor." By J. E. Marsh.

74. "Contributions to the knowledge of mucic acid. Part II. Action of phosphorus pentachloride on mucic acid." By S. Ruhemann, Ph.D., M.A., and W. J. Elliott, B.A.

75. "Contributions to the knowledge of mucic acid. Part III. Hydromuconic acid." By S. Ruhemann, Ph.D., M.A.

76. "Note on the reduction of aromatic amides." By A. Hutchinson, B.A., Scholar of Christ's College, Cambridge.

77. "Some improved vacuum joints and taps." By W. A. Shenstone.

78. "The production of camphor from turpentine." By J. E. Marsh, B.A., and R. Stockdale, B.A.

79. "*p*-Desylphenol." By Francis R. Japp, F.R.S., and G. H. Wadsworth, Associate of the Normal School of Science.

80. "Paraxylenesulphonic acids." By Gerald T. Moody, D.Sc., Demonstrator in the Chemical Department, City and Guilds of London Institute, Central Institution, and T. G. Nicholson.

81. "Action of phosphoric anhydride on fatty acids. Part II." By F. Stanley Kipping, Ph.D., D.Sc.

82. "An investigation of the conditions under which hydrogen peroxide is formed from ether. (Second Notice.)" By W. R. Dunstan and T. S. Dymond.

November 6th, 1890. Dr. W. J. Russell, F.R.S., President in the Chair.

Certificates were read for the first time in favour of Messrs. Gustavus Anthony Abrines, Waterport Street. Gibraltar; William Baxter, Fordingbridge, Hants; T. St. John Belbin, Bolton Mansions Hotel, South Kensington; John Thomas Brierley, 249, Bolton Road, Chorley, Lancashire; William J. Butcher, Emanuel College, Wandsworth Common; William Waters Butler, Elmdon, Selly Park, near Birmingham; Frank Brownsword, Heaton Moor, Stockport; M. Kelway Bamber, The Lodge, St. Waltham, Chelmsford; Ernest Bentz, 147, Bishop Street, Alexandra Park, Manchester; Arthur E. Barrows, Bloomfield Iron Works, Tipton, Staffordshire; W. E. B. Blenkinsop, 15, Earlsfield Road, Wandsworth Common; Thomas Arthur Cheetham, 29, Park Road, Glasgow; Arthur William Crosskey, Bentcliffe, Accrington; Arthur William Cooke, 15, Belle Vue Terrace, Leeds; Frederick Hudson Cox, 79, Angell Road, Brixton, S.W.; William L. Dudley, Nashville, Tennesee, U.S.A.; Thomas Edwards, Brewery House, Rhymney, Monmouthshire; Walter N. Edwards, 4, Herne Hill Road, S.E.; Thomas S. Goodwin, Montgomery Cottage, Newton, Glasgow; Alfred Henry Green, Oaklands, Lowton, Newton-le-Willows; William Mahowe Heller, St. Dunstan's College, Catford, S.E.; John C. Hewlett, Elmhurst, Beckenham, Kent; Charles Terry Holloway, Apsley Villa, Lewisham High Road, S.E.; John Richard Jackson, 51, Abbotsford Place, Glasgow; John

Jackson, Tredegar Road, Rhymney; Joseph Lunt, 5, South View, Eccleston Road, Ealing, W.; George Griffiths Leason, Ashfield Cottage, Stoke-on-Trent; Harry C. Myers, Strassburg, Germany; William Mackeay, 2, Victoria Mansions, Westminster, S.W.; Thomas Smith Murray, 7, Gayfield Square, Edinburgh; William Reginald Ormandy, Park Road, Newton-le-Willows; James Alexander Pond, Auckland, New Zealand; Thomas Platts, 7, Victoria Street, London; Henry Ramsen Redman, 10, The Gardens, Dulwich, S.E.; G. H. Robertson, 30, Hemstall Road, West Hampstead, N.W.; Charles William Seccombe, Church Park, Witchurch, Tavistock; Ernest Henry Sainter, 176, High Street, Redcar; J. Napier Spence, 9, Headstone Terrace, Harrow; Thomas Steel, Jarraville, Melbourne, Victoria; John Joseph Sudborough, 111, Stratford Road, Birmingham; Charles Thomas Sprayne, Reinsgraben, Göttingen; Francis Henry Tate, 9, Hackins Hey, Liverpool; John Cundall Wood, 32, Frederick Street, Sunderland; George Henry Wadsworth, 3, Southfield Square, Lamb Lane, Bradford; Sidney Wood, 5, Woodview, Bradford, Yorks; George Young, 5, Colinton Road, Edinburgh.

The following papers were read :—

83. "The magnetic rotation of saline solutions." By W. H. Perkin, Ph.D., F.R.S.

On account of the remarkable results given by solutions of the halhydrides and their compounds with ammonia and organic bases when examined as to their magnetic rotatory power (*cf. Chem. Soc. Trans.*, 1889, 740), it became important to study the solutions of metallic salts in a similar manner, and although the work which has been done in this direction is incomplete, and may occupy some time yet, the results, as far as they go, are of interest, especially in relation to the question of the condition of substances in solution. The substances which have been examined up to the present are chiefly chlorides, bromides, iodides, nitrates, a nitrite, sulphates and phosphates, also hydroxides of the alkali metals.

In the following comparisons, the values taken for the halogens are those found for them in their compounds with the alcohol radicles, *i.e.*, Cl = 1·733, Br = 3·562, I = 7·757. Those for the metals are deduced from the rotations of their nitrates, because in the case of ammonium nitrate it was found that this salt gave a rotation which was practically normal, and the salts of the metals have been found to behave in a similar manner to those of ammonium. Should there be any errors in these calculated values of the metals they will be but

small, and therefore will not materially influence the character of any deductions that may be made from the rotation of their compounds. They are Na = 0·558, K = 0·809, Li = 0·398, Ca = 0·691, Mg = 0·577.

The solutions examined were for the most part either saturated or supersaturated; in the case of sodium iodide, lithium nitrate and sodium hydroxide, two strengths, varying considerably from each other, were taken, but the results were found to be practically the same. In the case of lithium chloride, which forms much stronger solutions than any of the other chlorides, bromides or iodides examined, the rotation *increased* on dilution, as in the case of hydrogen chloride.

LiCl +	3·213	mol. OH_2 gave	4·166	mol. rot.
„ +	7·411	„ „	4·559	„
„ +	11·760	„ „	4·697	„

At present, this is the only salt known the rotatory power of which changes with the amount of water used, and probably, like hydrogen chloride, it will be found to give a stationary value before the above dilution of 11·760 mols. of water is reached; but further experiments must be made to establish the facts of the case.

In two instances the effect of varying temperature was tried. A solution of sodium bromide was examined at 16° and 78·5°; in this case there was a small reduction in the molecular rotation at the higher temperature of 0·105; with a solution of potassium iodide, examined at 16·6° and 84·4°, there was also a small diminution at the higher temperature, but only of 0·024. Substances, especially if they have high rotations, give a slightly lower rotation at higher temperatures like the above than at lower temperatures: so that, allowing for errors of observation, these results indicate that practically little or no change in the nature of the solutions took place when they passed from one temperature to another.

The following tables show the calculated and found rotations of the substances examined and their relationship to each other:—

Haloid Compounds.

	Calculated.	Found.	Ratio.
NaCl	2·291	5·068	1 : 2·212
KCl.....	2·542	5·377	1 : 2·115
LiCl.....	2·131	4·697	1 : 2·204
$CaCl_2$	4·157	9·085	1 : 2·185
$MgCl_2$	4·043	9·103	1 : 2·252

	Calculated.	Found.	Ratio.
NaBr	4·110	9·030	1 : 2·197
KBr.....	4·371	9·222	1 : 2·110
NaI.....	8·315	18·867	1 : 2·269
KI	8·566	18·690	1 : 2·182

It will be seen that the rotations of these salts, when in aqueous solution, are practically 2·2 times greater than the calculated values for the dry substance; they are even greater than those of the analogous ammonium compounds, the calculated values for which now given differ by 1 from those previously published, which were incorrect.

	Calculated.	Found.	Ratio.
NH_4Cl....	3·305	6·096	1 : 1·844
NH_4Br ...	5·134	10·196	1 : 1·985
NH_4I.....	9·329	19·996	1 : 2·144

A solution containing equimolecular proportions of NaI and NaOH gave a rotation for NaI = 18·454, or 0·413 lower than that given by the iodide alone.

Hydroxides of Alkali Metals.

	Calculated.	Found.	Ratio.
NaOH....	1·006	2·433	1 : 2·418
KOH.....	1·257	2·658	1 : 2·114

Here, again, a remarkable increase of rotation is obtained, quite as great, or even larger in one case, than with the halogen salts.

Potassium hydroxide in alcoholic solution gives a somewhat lower number than the above for its aqueous solution; but it is possible that some of the potassium in this instance may be in combination as alcoholate, and this may account for the difference.

Sulphates.

	Calculated.	Found.	Difference.
$NaHSO_4$	2·419	2·525	0·106
Na_2SO_4.....	2·513	2·877	0·364
Li_2SO_4.....	2·099	2·379	0·280

In this table the difference is given instead of the ratio, and it will be seen that it is but small compared with the foregoing, but it increases with the number of atoms of metal.

Phosphates.

	Calculated.	Found.	Difference.
NaH_2PO_4....	3·328	3·481	0·153
Na_2HPO_4....	3·678	4·076	0·398
Na_3PO_4.....	4·036	5·079	1·043

As in the case of the sulphates, the rotation increases beyond the calculated with the number of atoms of metal; in the last case the difference is considerable.

Potassium Nitrite.—This salt is interesting, because it allows of a comparison being made between it and potassium nitrate which can be placed side by side with a similar comparison between isobutyl nitrite and nitrate.

		Difference.
KNO_2.....	1·943	0·408.
KNO_3.....	1·535	
$C_4H_9NO_2$	5·510	0·330.
$C_4H_9NO_3$	5·180	

From this it is seen that in both cases the nitrites give larger rotations than the nitrates, and the differences do not vary very greatly, though sufficient to show that the rotation of potassium nitrate undergoes some change when that salt is in solution.

Nitrates.

$NaNO_3$	1·284
KNO_3	1·535
$LiNO_3$.....	1·124
$Ca(NO_3)_2$	2·143
$Mg(NO_3)_2$.....	2·029

It has been assumed that the solutions of the nitrates give practically normal results, and the values of the metals have been deduced from them: the reasons for this have already been given; it may be added that of all the salts examined the nitrates give the lowest numbers for the metals. Nevertheless, experiments are in progress to test the validity of this method of determining the values of the metals.

In considering the numbers given in this communication, it is well to remember that, owing to the method employed in calculating the results obtained from solutions, all experimental errors fall upon the numbers obtained for the dissolved substance, and consequently will also influence the differences found in comparing the results, as in the tables given above. When the solutions contain large percentages of dissolved substance the errors are but small, but when the

percentages are small the errors naturally increase; on this account it will be difficult to get good results with compounds that are sparingly soluble in water.

It is very difficult to understand why the haloid acids, their salts and also caustic alkalis should give such extremely large rotations when in aqueous solution. If dissociation takes place, there does not seem to be any reason why any very considerable change of rotation should occur; but whatever the cause, the change evidently indicates some very important difference existing between dissolved and undissolved substances of these classes.

Discussion.

Dr. Gladstone remarked that similar excessive values were obtained on determining the refractive powers of solutions of metallic chlorides, &c., although the difference between the calculated and observed values were much smaller than in the case of Dr. Perkin's measurements. It was all-important to determine the difference in the behaviour to light of a substance in its solid state and when in solution; but this was difficult, as few solids were uniaxial: as an example of the difference he mentioned that in the case of the sodium chloride the solid has a refraction of 14·4, while that of the dissolved substance is 15·3.

Mr. Pickering said that Dr. Perkin's results must have a very important bearing on the question of the nature of solutions. When salts caused a double depression of the freezing point, the physicists held it to be due to dissociation into ions; but here was a case of a similar effect which cannot well be attributed to dissociation. As far as can be seen, dissociation would not double the rotation, still less would it make it more than double, and, even if it could be held to do o, such an explanation would be inadmissible in the case of saturated solutions, for in such solutions the physicists themselves held that there is little or no dissociation.

Professor Ramsay thought that the abnormal results may not be entirely connected with dissociation into ions: the optical phenomena were probably much more complex; it was conceivable that the separated atoms might be much more powerfully affected in a magnetic field than when combined.

84. "Note on normal and isopropylparatoluidine." By E. Hori and H. F. Morley.

Desiring to distinguish with certainty between normal and isopropylparatoluidine, the authors have prepared the pure substances and several of their derivatives.

The normal compound boils at 230—233°; its density at 20° is 0·9243 gram per c.c., and at the boiling point 0·7543: hence its molecular specific volume is 197·53 (theory 199·5); its molecular refractive energy is 82·5 (theory 79·3).

Isopropylparatoluidine boils at 219—221 (uncorr.); its density at 20° is 0·9226 gram per c.c., and at the boiling point 0·7466: hence its molecular specific volume is 199·57; its molecular refractive energy is 81·4.

The isopropylnitrosamine is a crystalline solid, whereas the isomeride is an oil.

The normal and iso-compound form oxalates differing in solubility and stability.

85. "The action of light on ether in presence of oxygen and water." By Arthur Richardson.

In a recent paper by Professor Dunstan and Mr. Dymond (*Chem. Soc. Trans.*, 1890, 574) it is stated that hydrogen peroxide is not formed when pure ether is exposed to light in contact with air and water, and these authors consider that the formation of this substance is due to the impurities contained in the ether, which can be removed by treatment with potassium bichromate or iodhydric acid. The author describes experiments made with ether which had been purified by some of the methods described by Dunstan and Dymond; he finds that hydrogen peroxide is formed in the liquid in every case after exposure to light in contact with moist air or oxygen, but not in the dark at the ordinary temperature. The methods employed to prepare and purify the ether are described in full in the paper; they were as follows:—

(1.) Commercial "pure" ether, from which the alcohol had been removed by repeated shaking with water, was afterwards agitated with potassium bichromate.

(2.) Ether obtained by the action of pure sulphuric acid on pure alcohol was shaken with potash solution and with water, and one portion was treated with potassium bichromate, another with iodhydric acid.

(3.) The liquid from (2) was collected after exposure to light and again agitated with potassium bichromate.

(4.) Ether prepared from an entirely different sample of pure alcohol and pure sulphuric acid was treated as before with potassium bichromate; it was distilled after being allowed to stand over calcium chloride and then over metallic sodium. The ether boiled constantly at 34·6° at 760 mm. pressure corr. to 0°.

The ether prepared by these methods was placed in colourless bottles, and air or oxygen was passed into the space above the liquid before the stoppers were inserted.

Some experiments were made on the influence of temperature in bringing about the formation of hydrogen peroxide; it was found that ether and moist oxygen exposed to a temperature of 75—88° in the dark contained, after four days, considerable quantities of this substance; similar results were obtained when ether and oxygen were heated to 60° for a period of 40 hours. Ether vapour and moist oxygen gave practically no peroxide when so heated. It was found, however, that liquid ether kept at 0° contained hydrogen peroxide after exposure to light for four days.

Hence it appears that when special precautions are taken to ensure the presence of oxygen over the ether, hydrogen peroxide is formed at ordinary temperatures, and even at 0° in the light, but not in the dark; it is, however, formed in absence of light at about 60°.

Discussion.

Professor Dunstan said that Mr. Dymond and he had made their experiments on the conditions necessary for the formation of hydrogen peroxide from ether, because there was no evidence that previous workers had employed the pure substance. They had been unable to detect hydrogen peroxide in ether that had been exposed at a low temperature to the electric light and diffused daylight. For the detection of hydrogen peroxide, reliance had been placed on the characteristic chromic reaction which they had proved to be capable of indicating 0·0002 gram of the substance. Dr. Richardson, who meanwhile had purified ether by the method employed by the speaker, and still adhered to some of his original statements, asserted that he had detected hydrogen peroxide in ether exposed at a low temperature to white light by means of titanium oxide, but it appeared that he had failed to obtain the chromic reaction. The suggestions which Dr. Richardson had made to explain why hydrogen peroxide had not been formed in their experiments were quite untenable. At least 2 litres of air were in contact with the exposed ether. There could be no doubt as to the purity of the ether they had used. The slight greenish tint of the bottles was shown not to be detrimental by the circumstance that hydrogen peroxide was produced from specimens of impure ether contained in them. They had employed the electric light partly because they had failed to obtain results with diffused sunlight in London, and partly because they wished to ascertain whether pure ether was affected by violet rays acting at a low temperature. They had recently obtained evidence which seemed to show

that certain specimens of unpurified ether could form hydrogen peroxide even in the dark. The whole purport of Dr. Richardson's first paper on this subject was to prove that when hydrogen peroxide is formed from moist ether, the water and not the ether is oxidised. They had opposed this view as they were in possession of good evidence that the ether is oxidised. It now appeared that Dr. Richardson had abandoned his former view, although he still contended that hydrogen peroxide could be formed from water and oxygen alone in the presence of light. But they had also failed to confirm this statement. No evidence could be obtained of the presence of hydrogen peroxide in acidulated water which had been exposed to intense sunlight or to the electric light (*cf. Chem. Soc. Trans.*, 1890, 988). They were also unable to confirm the statement that pure ether yields hydrogen peroxide when heated with air and water to 50—60°.

Mr. Dymond said that Dr. Richardson had not stated whether he had tested his ether for the impurities which are known to be invariably present, some of which may be produced during the process of purification employed, and which are particularly difficult to remove, viz., aldehyde and ethylene. In his previous paper, Dr. Richardson had stated that after hydrogen peroxide had been produced in ether, the ether remained unaltered. Did he adhere to that statement now that he had convinced himself that the ether was concerned in the production of the peroxide? In the experiments made by Professor Dunstan and himself, it was always noticed that when peroxide of hydrogen was produced from ether, the ether afterwards contained aldehyde, acetic acid and other substances.

Mr. Groves, referring to Dr. Richardson's statement that he had found that pure dry ether was acted on when exposed with oxygen, said that this result was contrary to recent experience as to the influence of water in promoting chemical change; it was difficult to conceive how hydrogen peroxide could be produced in such a case.

Mr. Pickering inquired why so minute an amount of peroxide was obtained; if pure ether afforded hydrogen peroxide when oxidised, it was to be expected that the action would continue, and that a larger proportion would result.

Dr. Perkin said that the alcohol was best removed from ether by means of phosphoric anhydride. Dr. Japp mentioned that Professor Frankland had always used this substance in purifying the ether used in preparing zinc methide; and Professors Ramsay and Dunstan subsequently stated that they had employed it with good results.

Dr. Richardson, in reply, stated that he did not see that Professor Dunstan's ether had any claim to greater purity than that used by himself. On the contrary, the fact that Professor Dunstan's ether distilled

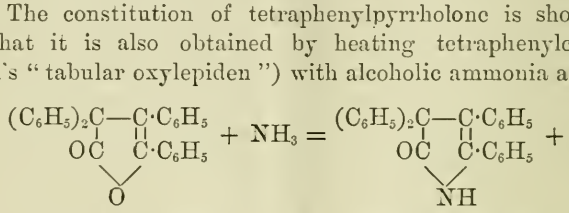
only within $\frac{1}{2}$ degree showed that it was not so pure as that used by him, which distilled within $\frac{1}{10}$ degree. The ether used by the speaker was found to be without action on potassium iodide in the dark after contact with the solution for two weeks. With regard to the remarks made on the quality of the bottles used, it appeared to him that the fact that methylated ether was found to contain H_2O_2 after exposure to light in greenish glass bottles, did not show that the formation of this body was in this case brought about by light at all, for, as Professor Dunstan had just pointed out, impure ether which had been kept in the dark was found to contain this substance. He did not see that the absence of H_2O_2 in Dunstan's ether could be accounted for by the use of the electric light, for Professor Dunstan states (*Chem. Soc. Trans.*, 1890, 579) that in one series ether was exposed for two months to much sunlight during August and September, the temperature ranging between 15—25°, but, under these circumstances, no H_2O_2 was formed. The speaker would like to point out that in all except the last sample of ether he had obtained sufficient H_2O_2 after exposure to give the blue coloration with $K_2Cr_2O_7$; in the last case, however, the time of exposure had been necessarily short, and the light exceedingly poor, so that the presence of H_2O_2 could only be detected by the more delicate tests such as KI and H_2TiO_3. He was not surprised to learn that Professor Dunstan had failed to obtain H_2O_2 on exposing H_2O to light, for in the formation of this body, under these conditions, many special precautions must be observed, such as keeping the temperature low, &c., as he found that the H_2O_2 first formed was very readily decomposed.

In reply to Professor Pickering, Dr. Richardson wished to point out that other products of decomposition were formed when ether was exposed to light, some of which might probably decompose the peroxide first formed; thus a specimen of ether which had been exposed with water and oxygen to light for 18 months contained no H_2O_2, the smell of the ether had changed, and black particles were seen floating in the liquid—this was a point which the author hoped to further investigate, however.

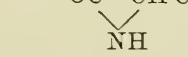
86. "Action of ammonia and methylamine on the oxylepidens." By Felix Klingemann, Ph.D., and W. F. Laycock, Ph.D.

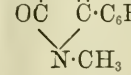
This investigation was undertaken with the object of ascertaining whether the analogy which was shown by Japp and Klingemann to prevail between the interactions of $\alpha\beta$-dibenzoylcinnamene and those of dibenzoylstilbene (Zinin's "acicular oxylepiden") was preserved in the behaviour of these compounds with ammonia and amines. The authors find that this is the case.

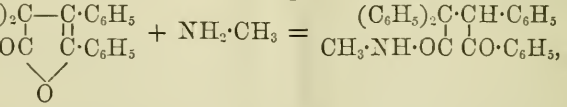
On heating dibenzoylstilbene with alcoholic ammonia at 200°, it is converted into a mixture of two isomeric compounds of the formula $C_{28}H_{21}NO$: *dibenzoylstilbenimide*, which crystallises from benzene in crusts of yellow, prismatic forms melting at 180—182°, and corresponds with dibenzoylcinnamenimide; and *tetraphenylpyrrholone*, which crystallises in pale-yellow, square plates melting at 206—207°, corresponding with triphenylpyrrholone. Dibenzoylstilbenimide is converted by heating at 310° into tetraphenylpyrrholone, just as dibenzoylcinnamenimide is converted into triphenylpyrrholone. The constitution of tetraphenylpyrrholone is shown by the fact that it is also obtained by heating tetraphenylcrotolactone (Zinin's "tabular oxylepiden") with alcoholic ammonia at 200° :—



Tetraphenylcrotolactone. Tetraphenylpyrrholone.

By the action of nascent hydrogen (from sodium and boiling amyl alcohol) tetraphenylpyrrholone is converted into *tetraphenylpyrrholidone*,  , which crystallises from alcohol in slender, pale-brown needles melting at 237°.

When dibenzoylstilbene is heated with an alcoholic solution of methylamine at 200°, it is converted, with elimination of water, into *methyltetraphenylpyrrholone*,  , which crystallises from hot alcohol in thin, faintly yellowish, asymmetric plates melting at 161°.

On the other hand, tetraphenylcrotolactone unites directly with methylamine at 150°, forming *benzoyltriphenylpropiomethylamide*,  , which crystallises from glacial acetic acid in lustrous plates melting at 267°. When this compound is distilled under reduced pressure, it parts with water and is converted into methyltetraphenylpyrrholone. The crystalline form of the compound thus obtained differed, however, from that of the same substance from dibenzoylstilbene, and the melting point was found at 158°, instead of at 161° ; but the authors

attribute these differences to dimorphism, as in the case of the corre-corresponding triphenyl derivatives prepared by Japp and Klinge-mann.

87. "Condensation of acetone-phenanthraquinone." By G. H. Wadsworth.

The author finds that by the dehydrating action of a mixture of concentrated sulphuric acid and absolute alcohol, acetone-phenanthra-quinone is converted into a compound of the formula $C_{34}H_{22}O_3 = 2C_{17}H_{14}O_3 - 3H_2O$. It crystallises from benzene in tufts of minute needles melting at 238° C.

88. "Contributions to the knowledge of mucic acid. Part IV. Action of phosphorus pentachloride on mucic acid." By S. Ruhemann, Ph.D., M.A., and S. F. Dufton, B.A., B.Sc.

The authors find that mucic acid is converted by the action of phosphorus pentachloride into a crystalline compound which, assuming dichloromuconic acid to be an acid of the formula $\begin{matrix}CCl{\cdot}CH{\cdot}COOH\\ |\\ CCl{\cdot}CH{\cdot}COOH\end{matrix}$, may be represented by the formula $\begin{matrix}CCl(POCl_2){\cdot}CH(OH){\cdot}COCl\\ |\\ CCl(POCl_2){\cdot}CH(OH){\cdot}COCl\end{matrix}$. On dissolving this substance in water and carefully concentrating the solution, large, colourless, rhombic crystals of the corresponding *phosphodichloromuconic acid* are obtained; several salts of this acid are described, among others, one formed by the combination of $6NH_3$ with the acid. The phosphochloride is converted by the action of phosphorus pentachloride at 120° into dichloromuconyl chloride, hydrogen chloride and phosphorus oxychloride.

The authors have succeeded in converting the isomeride of Bode's dichloromuconic acid discovered by Ruhemann and Elliott (*cf.* Trans., 1890, 931) into Bode's acid, by adding a small quantity of bromine to the cold aqueous solution; they therefore conclude that the isomeric dichloromuconic acids are related to each other much as are maleic and fumaric acids.

89. "Halogens and the asymmetrical carbon atom." By F. H. Easterfield.

At the suggestion of Professor Emil Fischer, the author has endeavoured to prepare active haloid derivatives similar in constitu-tion to Le Bel's optically active secondary amyl iodide, $CH_3{\cdot}CHI{\cdot}C_3H_7$,

which at present stands alone as the only active compound in which a halogen is united to the asymmetric carbon atom. His results are negative. Thus active mandelic acid gave inactive phenylbromacetic acid when heated with bromhydric acid at a temperature not exceeding 50°; and no resolution of the acid into active constituents was effected by means of alkaloid salts.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Manual of Pharmaceutical Testing, by B. S. Proctor. London 1890. From the Publishers.

A Treatise on Practical Chemistry and Qualitative Analysis, by F. Clowes. 5th Edition. London 1890. From the Author.

A Technological Dictionary of Insurance Chemistry, by W. A. Harris. Liverpool 1890. From the Author.

Principles of General Organic Chemistry, by E. Hjelt. Translated by J. B. Tingle. London 1890. From the Translator.

Geological Survey of New South Wales:—

Palæontology, No. 3. Geological and Palæontological Relations of the Coal and Plant-bearing Beds of the Palæozoic and Mesozoic Age in Eastern Australia and Tasmania, by O. Feistmantel.

Palæontology, No. 4. The Fossil Fishes of the Hawkesbury Series at Gosford, by A. S. Woodward. 4to. Sydney 1890.

From the Director of the Survey.

United States Geological Survey:—

Eighth Annual Report (in 2 parts). 1886–7. 4to. Washington 1889.

Monographs, XV (2 parts). The Potomac or Younger Mesozoic Flora, by W. M. Fontaine.

Monographs, XVI. The Palæozoic Fishes of North America, by J. S. Newberry. 4to. Washington 1889.

From the Director of the Survey.

A Course of Chymistry, by N. Lemery. Translated from the French (2nd Edition) by W. Harris. London 1686.

Trois Traitez de la philosophie naturelle, non encore imprimez. Le Sécret livre du tres-ancien Philosophe Artephius, traitant de l'Art occulte de transmutation Métallique. Les figures hiéroglifiques de Nicolas Flamel ainsi qu'il les a mises en la quatriesme arche qu'il a bastie au Cimetière des Innocents à Paris. Le vrais

livre du docte Synesius. Le tout traduit par P. Arnauld. Paris 1612. From T. Bolas, Esq.

Qualitative Chemical Analysis of Inorganic Substances, by C. F. Juritz. Cape Town 1890. From the Author.

The Organic Analysis of Potable Waters, by J. A. Blair. London 1890. From the Publishers.

Chemical Arithmetic. Part I. A collection of Tables for the use of Chemists and others, by W. Dittmar. Glasgow 1890. From the Publishers.

Manual of Assaying Gold, Silver, Copper, and Lead Ores, by W. L. Brown. Revised and enlarged by A. B. Griffiths. London 1890. From the Publishers.

Grundzüge der theoretischen Chemie, von L. Meyer. Leipzig 1890. From the Author.

Pamphlets.

Report of the Field Experiments on Swedes with different Manures, proposed to members of the Royal Agricultural College Club; by E. Kinch. Cirencester 1890. From the Author.

Die Licht- und Wärmestrahlung verbrennender Gase, von R. von Helmholtz. 4to. Berlin 1890. From the Author.

Ueber Feuerbestattung, von F. Goppelsroeder. Mühlhausen i. Els. 1890. From the Author.

Studier öfver Gadolinit, af G. W. Petersson. Stockholm 1890.

Kemiska Studier öfver Nagra Hartser, af K. A. Vesterberg. Upsala 1890. From the Author.

Nitrogen, its Uses and Sources in Agriculture, by C. M. Aikman. Glasgow 1890. From the Author.

Sull' influenza della qualità delle Acque usate nella trattura dei bozzoli, del E. Rotondi. Roma 1890. From the Author.

Results of Experiments at Rothamsted on the Growth of Leguminous Crops for many years in succession on the same land, by J. H. Gilbert. (From the Agricultural Student's Gazette, N. S., vol. IV, 5 and 6). Cirencester 1890. From the Author.

Gold from Pyrites and other Sulphides, by E. J. Hill. Dunedin 1890. From the Author.

Production de variétés chez les Saccharomyces, par E. C. Hansen (Extrait des Annales de Micrographie II, 5), 1890.

Nouvelles recherches sur la circulation du Saccharomyces apiculatus dans la Nature, par E. C. Hansen (Extrait des Annales des Sciences Naturelles: Botanique, XI, 3). 1890.

Ueber die Pilzstudien in der Zymotechnik, von E. C. Hansen (Abdruck aus der Zeits. f. das gesammt Brauwesen). 1890. From the Author.

Wattles and Wattle-Barks, by J. H. Maiden. Sydney 1890. From the Author.

Richesse de Vesous et Cannes à l'Ile Maurice, par L. Ehrmann. Sèries I et II, 1888–90 (Extraits de la Revue Agricole). Maurice 1889–90. From the Author.

The Chemical Constitution of some Colonial Fodder Plants and Woods, by C. F. Juritz. Wynberg 1890. From the Author.

Address on Technical Education, by J. Philipson. Aberdeen 1890. From the Author.

International Standards for the Analysis of Iron and Steel. Extracts from the work of the American Committee, by J. W. Langley. (From the Trans. of the American Inst. of Mining Engineers, October, 1890.)

II. *By Purchase.*

La coloration artificielle des vins, par M. Monavon. Paris 1890.

La glycogénie animale, par J. Seegen. Traduction par L. Hahn. Paris 1890.

Cours de Minéralogie, par A. de Lapparent. 2me. Edition. Paris, 1890.

Études cristallographiques, par A. Bravais. Paris 1866.

The Study of Rocks, by F. Rutley. 4th Edition. London 1888.

A System of Mineralogy. Descriptive Mineralogy, comprising the most recent Discoveries, by J. D. Dana, aided by G. J. Brush. 9th Edition. New York 1889.

Tabellarische Uebersicht der Mineralien nach ihren krystallographisch-chemischen Beziehungen geordnet, von P. Groth. 3te Aufl. Braunschweig 1889.

Die mikroscopische Beschaffenheit der Mineralien und Gesteine, von F. Zirkel. Leipzig 1873.

Die Paragenesis der Mineralien, von A. Breithaupt. Freiberg 1849.

Lehrbuch der Mineralogie, von G. Tschermak. 3te Aufl. Wien 1889.

Elemente der Mineralogie, begründet von C. F. Naumann. 12te Aufl., bearbeitet von F. Zirkel. Leipzig 1885.

Lehrbuch der chemischen und physikalischen Geologie, von G. Bischof. Bde. I—III and Suppl. 1863–66 and 1871.

Tafeln zur Bestimmung der Mineralien, von F. Kobell. 12te Aufl., bearbeitet von K. Oebbeke. München 1884.

A meeting of the Research Fund Committee will be held in December. Fellows desiring grants are requested to forward their applications to the Secretaries.

At the next meeting, on November 20th, there will be a ballot for the following candidates:—

1. Branson Charles F., Kenley Lodge, Macaulay Road, Clapham Common.
2. Clark, D. G., 44, St. John's Wood Park, N.W.
3. Caird, George, 20, Springfield, Dundee.
4. Colman, Walter Henry, 41, Poynings Road, Junction Road, N.
5. Day, Charles Edwin, 1, Merchiston Bank Terrace, Edinburgh.
6. Edward, John Huchison, 117, Stockport Road, Manchester.
7. Frost, Robert, St. James's Chambers, Duke Street, S.W.
8. German, George, Huntingdon House, Ashby-de-la-Zouch.
9. Gordon, Colin, Millwall Club, West Ferry Road, Millwall.
10. Haslam, Arthur R., Ph.D., 64, Rathgar Road, Dublin.
11. Haydon, Frank, Ettrick, Putney Common, S.W.
12. Johnson, John Robert, 16, Oxford Street, Liverpool.
13. Jenkins, Wallace, 410, Glossop Road, Sheffield.
14. Kelly, Patrick, 43, Lennox Street, Dublin.
15. McKillopp, John, Pulan Brani, Singapore.
16. Marshall, Thomas Rhymer, 4, East Castle Road, Edinburgh.
17. McCubbin, William Alexander, Mill Bank House, West Derby, Liverpool.
18. Palmer, Arthur E., Ashley Mount, Tettenhall, Wolverhampton.
19. Parker, Thomas, M.I.C.E., Wolverhampton.
20. Parkes, Thomas, Grammar School, Stamford.
21. Redding, Richard James, Royal Laboratory, Woolwich Arsenal.
22. Seaton, Edward Cox, 35, George Street, Hanover Square.
23. Smith, Frederick, Johannesburg, Transvaal, South Africa.
24. Stagg, William, 52, Seymour Road, Bristol.
25. Thornley, John Brooks, Ivanhoe Terrace, Ashby-de-la-Zouch.
26. Wilson, James Mitchell, Hall Gate, Doncaster.

The following papers will be read :—

"The estimation of cane-sugar." By C. O'Sullivan, F.R.S., and F. W. Tompson.

"A new method of determining the specific volumes of liquids and of their saturated vapours." By Professor S. Young.

"The molecular weights of metals when in solution." By Messrs. Heycock and Neville.

"The spectra of blue and yellow chlorophyll with some observations of leaf green." By Professor Hartley, F.R.S.

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Issued 26/11/1890.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 88. Session 1890–91.

ember 20th, 1890. Dr. W. J. Russell, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. Arthur Colefax, B.A., Ph.D., Ashgrove, Bradford, Yorkshire; Ernest F. Hooper, Elmley, Beckenham; Moses William Jones, 343, Aspen Terrace, Church, Lancashire; Stephen Newcome Wellington, Riverdale House, Brundall, Norfolk; Thomas M. Wyatt, 20, Queen Square, W.C.; David Wilkinson, Dunedin, Otago, New Zealand.

The following were elected Fellows of the Society:—Messrs. Charles F. Branson; D. G. Clark; Charles Edwin Day; Robert Frost; Colin Gordon; Arthur R. Haslam, Ph.D.; Wallis Jenkins; John McKillop; Thomas Rhymer Marshall; William Alexander McCubbin; Thomas Parkes; Richard James Redding; Edward Cox Seaton; Frederick Smith; John Brooks Thornley; and James Mitchell Wilson.

The following papers were read:—

90. "A new method of determining the specific volumes of liquids, and of their saturated vapours." By Sydney Young, D.Sc., Professor of Chemistry, University College, Bristol.

When a tube closed at both ends and partly filled with a liquid is raised in temperature, the liquid expands, but the apparent expansion is less than the real, for a certain amount of the substance separates and occupies the space above the liquid in the form of saturated vapour. If the density of the vapour were known it would be possible to apply the necessary correction; but at high temperatures

and pressures this is not the case. If, on the other hand, the upper part of the tube (enclosing the vapour and a portion of the liquid) be heated to a high temperature, the lower part being kept at a constant low temperature, and if, subsequently, a greater length of the tube be heated to the high temperature, there will again be expansion; but in this case the observed expansion will be greater than the real, for in consequence of the diminution in volume of the saturated vapour, a portion of it must have condensed.

In both cases we have the same two unknown values, the true volume of the liquid and the specific volume of the vapour, and from the two equations involving the experimental data, it is, therefore, possible to calculate both values.

The experimental method, based on the principles just described, is described in full in the paper. It possesses the following advantages:—It is applicable to substances such as nitrogen peroxide or bromine which attack mercury; it is available for a very wide range of temperature and pressure, even to the critical points of many substances; the data obtained serve to determine not only the specific volume of the liquid but also that of its saturated vapour.

91. "The molecular condition of metals when alloyed with each other." By C. T. Heycock and F. H. Neville.

In the Journal of the Chemical Society for May, 1890, we showed that 1 atomic proportion of a metal when dissolved in tin produces the fall in the freezing point that on the theory of osmotic pressure should be produced by one molecular proportion: we therefore concluded that when metals are dissolved in tin their molecules are monatomic. During the past summer we have succeeded in carrying out similar experiments, using bismuth, cadmium and lead as solvents. The method of experimenting was practically the same as for tin. We now give a brief abstract of our results. The molecular falls predicted by the theory of osmotic pressure, that is, the falls that one *molecular* proportion of any substance ought to produce when dissolved in 100 atomic proportions of the solvent metal, are as follows:—

Solvent bismuth,	mol. fall is	2·08°	C.
Solvent cadmium	,,	4·5°	C.
Solvent lead	,,	6·5°	C.

Hence, the following tables show that the atom is identical with the molecule in many cases:—

Bismuth.

	No. of experiments.	No. of atoms per 100 atoms Bi.	Mean atomic fall.
Lead	20	1·1—1·75	2·1
Thallium	2	0·3—0·9	2·07 M.
Mercury	4	0·3—4·3	2·04
Tin	4	0·16—2·2	2·03. Steady.
Palladium	4	0·9—2·2	2·03
Platinum	6	0·2—1·2	2·02. Steady.
Cadmium	4	1·0—4·0	2·01
Gold	4	0·4—1·8	1·97
Sodium	3	0·8—4·0	1·94. Steady.
Silver	3	0·7—2·5	1·91
Zinc	4	1·3—4·8	1·6
Copper	5	0·23—0·6	1·23
Arsenic	5	0·25—2·3	0·68. Very steady.
It is noticeable that arsenic both in bismuth and cadmium gives $\frac{1}{3}$ fall.			
Antimony	3	0·23—1·0	2·79. Rise.

Cadmium as a Solvent.

	No. of experiments.	No. of atoms per 100 atoms Cd.	Mean atomic fall.
Antimony	2	0·3—0·5	4·71 M.
Platinum	2	0·08—0·13	4·55
Bismuth	4	0·05—0·5	4·58
	3	2·2—3·6	4·09
Tin	2	0·66—2·6	4·48
Sodium	3	0·6—1·3	4·44
Lead	2	0·84—1·4	4·4
Thallium	3	0·24—1·28	4·34 M.
Copper	8	0·2—2·0	3·5. No falling off.
Mercury	3	0·23—0·68	2·77
Zinc	3	0·06—1·6	2·72. No falling off.
Palladium	3	0·13—0·26	2·35
Potassium	2	0·5—0·6	2·26 M.
Gold	3	0·14—0·7	1·48
Arsenic	1	0·2	1·6

Seven out of fourteen metals appear to have monatomic molecules, the osmotic pressures ranging from 2 to more than 40 atmospheres. In the case of zinc, palladium and mercury, there is a smaller fall even at the low pressure of 2—8 atmospheres.

Arsenic gives a fall of $\frac{1}{3}$.

Silver	1	0·05	9·33 Rise.

The dissolved substance separates from the solution as temperature falls.

Lead.

	No. of experiments.	No. of atoms per 100 atoms of Sn.	Mean atomic fall.	
Gold	4	0·33—2·7	6·45.	Steady.
Palladium	3	0·32—1·8	6·45	
Silver	6	0·2—1·4	6·45	
Platinum	4	0·15—0·6	6·42	
Copper	3	0·1—0·195	6·15	
Arsenic	4	0·38—4·9	5·33	
Magnesium	2	1·5	4·56	
Zinc	3	0·2—1·2	4·43	
Antimony	4	0·6—4·7	3·9.	Steady.
Cadmium	2	0·6—6·1	3·62	Steady.
Mercury	3	0·73—6·7	3·31	½
Bismuth	6	0·23—4·6	3·02	Steady.
Tin	3	0·4—1·8	1·8	¼ Sn_4.
	2	6·0—9·0	1 6	
Sodium	2	—	1·06 ?	

Theoretical fall = 6·5.

Of the fourteen metals dissolved in lead, it would appear that five have monatomic molecules; while mercury, bismuth and cadmium are diatomic; the molecule of tin would seem over a long range to be tetratomic.

92. "The estimation of cane-sugar." By C. O'Sullivan, F.R.S., and Frederic W. Tompson.

The authors describe a new method of estimating sucrose which they claim is applicable to all solutions containing cane-sugar, including natural juices and other preparations in which the use of acids is not possible. The process is a very simple one, and it is shown, by comparing it with estimations in which invertase is used, that it is very accurate. It is based on the one used by Kjeldahl in 1881, and is as follows:—

The neutral solution containing cane-sugar is placed in a constant temperature bath at 55°. A little pressed brewer's yeast is added, and complete admixture secured by gentle stirring. At the end of four hours inversion is nearly always finished. The solution is cooled, made up to double its original bulk and filtered. During the process there is a decrease in the optical activity of the solution, and an increase in the cupric reducing power. Each of these factors is an accurate measure of the amount of cane-sugar originally present. The authors quote experiments showing that good results are thus obtained in solutions which would not admit of the use of acids.

93. "The spectra of blue and yellow chlorophyll, with some observations on leaf-green." By W. N. Hartley, F.R.S.

The author refers to the numerous memoirs on chlorophyll of Stokes, Sorby, Chautard, Timiriaseff, Pringsheim, Reinke and of Russell and Lapraik and Schunck. Having been occupied at various times during the last seven years in an investigation of the different colouring matters described under the name of chlorophyll, he has deemed it advisable to present his results to the Society without awaiting the further development of the research. The subject-matter may be conveniently arranged under the following heads:—

a. Observations on the spectrum of chlorophyll contained in living tissues.
b. The spectrum of chlorophyll as seen in dried leaves.
c. Mode of extracting leaf-green unchanged and separating the blue from the yellow chlorophyll.
d. Measurements of the spectra of the chlorophylls.

1. Living tissues which are fresh and young and which, therefore, contain the leaf-green unaltered exhibit no trace of a band in the yellow close to D, such as is usually attributed to chlorophyll, and there is no indication of one in the green. Complete absorption, just beyond *b*, extends through the ultra-violet.

2. *Yellow chlorophyll* has a distinct absorption-band in the red differing from that of *blue chlorophyll*. It has likewise a distinct fluorescence.

3. When light is concentrated on living tissues the absorption spectrum of the green colouring matter is soon altered.

4. Separation of *blue* from *yellow chlorophyll*. The *blue chlorophyll* may be extracted from minced leaves by cold absolute alcohol, and may be precipitated by addition of baryta. The *yellow chlorophyll* is not so precipitated, or not precipitated so readily.

A warm solution of boracic acid in glycerine, mixed with a little alcohol, liberates the unchanged blue chlorophyll from the dried barium compound.

5. The *blue chlorophyll* exhibits two absorption-bands in the red, close together; in the less refrangible region of rays one overlies B and the other overlies C. There is a feebler band near D.

6. Concentrated solutions of *yellow chlorophyll* in benzene are brownish in colour, and exhibit a magnificent red fluorescence.

7. When *blue* and *yellow chlorophyll* are separately treated with formic acid and ether, there are produced two new substances showing absorption-bands in the green. It is believed that when these bands have been observed, either in preparations of chlorophyll or in

living tissues, that the chlorophyll has been altered by oxidation of formic aldehyde in the plant. This oxidation could be caused in living tissues by an excessive degree of illumination, which causes the destruction of the tissues, and otherwise by exposure of the contents of the plant cells to air or oxygen. An excessive illumination causes an exceedingly great activity in decomposing carbonic acid, and probably oxygen cannot be respired sufficiently rapidly; hence there may be a reverse action, or an oxidation of formic aldehyde to formic acid.

8. The leading characteristics of unaltered leaf-green are those of *blue chlorophyll*, namely, an intense absorption in the red, stronger even than in the violet or ultra-violet.

94. "Note on dibenzanilide." By J. B. Cohen, Ph.D.

In consequence of the appearance of the papers of Paal and others, and of Pictet (*Berichte*, 1890, 2587 and 3011), the author describes the results of experiments made some time ago. He comes to the conclusion that up to the present dibenzanilide has not been prepared; at any rate, not in the pure state. He finds that on heating benzanilide with acetic anhydride and a small quantity of fused sodium acetate, it is converted into acetanilide.

ADDITIONS TO THE LIBRARY.

By Purchase.

Lehrbuch der organischen Chemie, von V. Meyer und P. Jacobsen. Band I, Hälfte 1. Leipzig 1890.

La Révolution chimique: Lavoisier, par M. Berthelot. Paris 1890.

Das Fahlberg'sche Saccharin (Anhydro-orthosulfaminbenzoësäure), von R. Stutzer. Braunschweig 1890.

Universal-Pharmakopöe, von B. Hirsch. Band II. Göttingen, 1890.

Handbuch der Photographie, von H. W. Vogel. I. Theil: Die Photochemie. Berlin 1890.

Lehrbuch der technischen Chemie, von H. Ost. Berlin 1890.

Lehrbuch der chemischen Untersuchungs-Methoden zur Diagnostik innerer Krankheiten, von F. Wiesener. Berlin 1890.

Geschichte des Zuckers, von E. O. von Lippmann. Leipzig 1890.

Einführung in das Studium der theoretischen Chemie, von. A. Rossing. München und Leipzig, 1890.

Die Bacteriologie in ihren Beziehungen zur Landwirthschaft, von E. Kramer. Theil I: Die in der Landwirthschaft durch Bakterien bewirkten Vorgänge. Wien 1890.

I. Ueber Aufnahme und Ausgabe ungelöster Körper. II. Zur Kenntniss der Plasmahaut und der Vacuolen, nebst Bemerkungen über den Aggregatzustand des Protoplasmas und über osmotische Vorgänge, von W. Pfeffer (aus Bd. XVI der Abth. der k. Sächs. Ges. der Wissen.). Leipzig 1890.

Berichte der Versuchsstation für Zuckerrohr in West-Java. Heft I. Dresden 1890.

Gas-analytische Methoden, von W. Hempel. 2te Aufl. Braunschweig 1890.

A meeting of the Research Fund Committee will be held in December. Fellows desiring grants are requested to forward their applications to the Secretaries before December 13th.

At the next meeting, on December 4th, there will be a ballot for the following candidates :—

1. Abrines, Gustavus Anthony, Waterport Street, Gibraltar.
2. Baxter, William, Fordingbridge, Hants.
3. Belbin, T. St. John, Bolton Mansions Hotel, South Kensington.
4. Brierly, John Thomas, 249, Bolton Road, Chorley, Lancashire.
5. Butcher, William J., Emanuel College, Wandsworth Common.
6. Butler, William Waters, Elmdon, Selly Park, near Birmingham.
7. Brownsword, Frank, Heaton Moor, Stockport.
8. Bamber, M. Kelway, The Lodge, St. Waltham, Chelmsford.
9. Bentz, Ernest, 147, Bishop Street, Alexandra Park, Manchester.
10. Barrows, Arthur E., Bloomfield Iron Works, Tipton, Staffordshire.
11. Blenkinsop, W. E. B., 15, Earlsfield Road, Wandsworth Common.
12. Cheetham, Thomas Arthur, 29, Park Road, Glasgow.
13. Crosskey, Arthur William, Bentcliffe, Accrington.
14. Cooke, Arthur William, 15, Belle Vue Terrace, Leeds.
15. Cox, Frederick Hudson, 79, Angell Road, Brixton, S.W.
16. Dudley, William L., Nashville, Tennesee, U.S.A.
17. Edwards, Thomas, Brewery House, Rhymney, Monmouthshire.
18. Edwards, Walter N., 4, Herne Hill Road, S.E.

19. Goodwin, Thomas S., Montgomery Cottage, Newton, Glasgow.
20. Green, Alfred Henry, Oaklands, Lowton, Newton-le-Willows.
21. Heller, William Mahowe, St. Dunstan's College, Catford, S.E
22. Hewlett, John C., Elmhurst, Beckenham, Kent.
23. Holloway, Charles Terry, Apsley Villa, Lewisham High Road. S.E.
24. Jackson, John Richard, 51, Abbotsford Place, Glasgow.
25. Jackson, John, Tredegar Road, Rhymney.
26. Lunt, Joseph, 5, South View, Eccleston Road, Ealing, W.
27. Leason, George Griffiths, Ashfield Cottage, Stoke-on-Trent.
28. Myers, Harry C., Strassburg, Germany.
29. Mackeay, William, 2, Victoria Mansions, Westminster.
30. Murray, Thomas Smith, 7, Gayfield Square, Edinburgh.
31. Ormandy, William Reginald, Park Road, Newton-de-Willows.
32. Pond, James Alexander, Auckland, New Zealand.
33. Platts, Thomas, 7, Victoria Street, London, S.W.
34. Redman, Henry Ramsen, 10, The Gardens, Dulwich, S.E.
35. Robertson, G. H., 30, Hemstall Road, West Hampstead.
36. Seccombe, Charles William, Church Park, Whitchurch, Tavistock.
37. Sainter, Ernest Henry, 176, High Street, Redcar.
38. Spence, J. Napier, 9, Headstone Terrace, Harrow.
39. Steel, Thomas, Jarraville, Melbourne, Victoria.
40. Sudborough, John Joseph, 111, Stratford Road, Birmingham.
41. Sprayne, Charles Thomas, Reinsgraben, Göttingen.
42. Tate, Francis Henry, 9, Hackins Hey, Liverpool.
43. Wood, John Cundall, 32, Frederick Street, Sunderland.
44. Wadsworth, George Henry, 3, Southfield Square, Lamb Lane, Bradford.
45. Wood, Sidney, 5, Woodview, Bradford, Yorks.
46. Young, George, 5, Colington Road, Edinburgh.

The following paper will be read:—

"The volumetric estimation of titanium." By Dr. B. Brauner.

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Issued 13/12/1890.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 89. Session 1890–91.

December 4th, 1890. Dr. W. J. Russell, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. Charles Henry Corbett, Barnard Castle; Hendrick Thomas Donovan, Crumpton Street, Bridgetown, Barbadoes; Henry Charles Jenkins, Lorne Villa, Iveson Road, Hampstead; William Morley Martin, Cardrew, Redruth; Arnold Whitaker Oxford, 8, Henrietta Street, Cavendish Square, W.; Frederick William De Velling, High Street, Heckmondwike, Yorkshire; Herbert D. Shaw, Castle Mount, Sandal, nr Wakefield; R. Stockdale, The Grammar School, Leeds: Kenelm Edward Symes, Magdalen House, Bridport, Dorset.

The following were elected Fellows of the Society:—Messrs. Gustavus Anthony Abrines; John Thomas Brierley; William J. Butcher; William Waters Butler; Frank Brownsword; M. Kelway Bamber; Ernest Bentz; W. E. B. Blenkinsop; Thomas Arthur Cheetham; Arthur William Crosskey; Arthur William Cooke; William L. Dudley; Thomas S. Goodwin; Alfred Henry Green; William Mahowe Heller; John Richard Jackson; Joseph Lunt; Harry C. Myers; William Mackeay; Thomas Smith Murray; William Reginald Ormandy; James Alexander Pond; Thomas Platts; G. H. Robertson; Ernest Henry Sainter; Thomas Steel; John Joseph Sudborough; Charles Thomas Sprayne; Francis Henry Tate; George Henry Wadsworth; Sidney Wood; George Young.

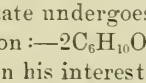
The following papers were read:—

95. "The action of heat on ethylic β-amidocrotonate." Part I. By J. Norman Collie, University College, London.

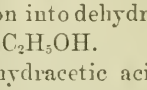
Some years ago, whilst working with ethylic β-amidocrotonate, the

author noticed that during its purification by distillation under reduced pressure a crystalline compound of the formula $C_{10}H_{13}NO_3 = 2C_6H_{11}NO_2 - NH_3 - C_2H_6O$ was always produced in small quantities, and remained behind in the fractionating flask. This condensation product was found to be the ethylic salt of an acid $C_8H_9NO_3$, which from its properties was considered to be the monocarboxylic acid of a hydroxylutidine. Owing to the small quantities obtained, the investigation was carried no further. Since then, having had to work with large amounts of ethylic β-amidocrotonate, a further supply of the condensation compound has been obtained, and a more exact study of its derivatives has been possible. The author now finds that the acid is *not* a hydroxyl derivative of lutidine, but *lutidonemonocarboxylic acid*, for on heating it yields carbon dioxide and lutidone or $\alpha\alpha'$-dimethylpyridone. This partial decomposition by heat of ethylic β-amidocrotonate is therefore very similar to that which ethylic acetoacetate undergoes in its conversion into dehydracetic acid during distillation:—$2C_6H_{10}O_3 = C_8H_8O_4 + 2C_2H_5OH$.

Feist in his interesting paper on dehydracetic acid (*Annalen*, **257**, 253) has shown that it is easily converted into dimethylpyronecarboxylic acid, the oxygen analogue of dimethylpyridonecarboxylic acid:—



Dimethylpyronecarboxylic acid.



Dimethylpyridonemonocarboxylic ethyl ether.

Ethylic lutidonemonocarboxylate does not decompose when boiled with caustic soda, but is merely hydrolysed and converted into the sodium salt of the acid; with phenylhydrazine and hydroxylamine it also does not form any compounds, and thus differs from dehydracetic acid. With bromine it forms a monobrominated derivative, $C_{10}H_{12}NO_3Br$, and with pentachloride of phosphorus the compound $C_{10}H_{12}NO_2Cl$. The acid obtained from the sodium salt melts at 247° C., decomposing at the same time into carbon dioxide and a compound which agrees in every respect with the $\alpha\alpha'$-dimethylpyridone, C_7H_9NO, obtained by Haitinger from dehydracetic acid, and also by Conrad and Gentzeit by heating lutidonedicarboxylic acid. This lutidone when heated with zinc-dust yields, according to Haitinger, $\alpha\alpha'$-dimethylpyridine boiling at 148—151° C., whilst the $\alpha\alpha'$-dimethylpyridine obtained from other sources boils at 142—143° C. Conrad and Gentzeit also obtained a lutidine from this lutidone, but do not give its boiling point. The author has been able to obtain a lutidine by four different methods:—

(1.) By distillation of the potassium salt of lutidonecarboxylic acid with excess of solid caustic potash.

(2.) By the prolonged action of nascent hydrogen (from tin and hydrochloric acid) on the chlorolutidine obtained by treating the lutidone with pentachloride of phosphorus.

(3.) By heating the chlorolutidine with zinc-dust in an atmosphere of hydrogen.

(4.) By heating the chlorolutidine obtained from dehydracetic acid by Haitinger's method with zinc-dust.

All these four methods gave a lutidine boiling at 144—145° C., and yielding a platinum salt melting at 210—212° C., the melting point found by Epstein and Ladenburg for the chloroplatinate of $\alpha\alpha'$-dimethylpyridine. The author has also been able to compare this lutidine with a lutidine boiling at 143—144° obtained by Professor Ramsay from bone oil, and is led to regard it as identical therewith. By oxidation of the lutidine from ethylic β-amidocrotonate with potassium permanganate, a pyridinedicarboxylic acid was obtained melting at 235° C. (corr.), which, on heating, gave pyridine, showing that it was dipicolinic or $\alpha\alpha'$-pyridinedicarboxylic acid.

96. "The action of heat on nitrosyl chloride." By J. J. Sudborough, B.Sc. (Lond.), and G. H. Miller.

An account is given of a series of determinations of the vapour-density of nitrosyl chloride, NOCl, at various temperatures. At temperatures from 15° to 693°, the values obtained so nearly coincide with the theoretical value 32·67, that it is to be supposed that no dissociation takes place below about 700°. At higher temperatures, the compound is no longer stable, as the following numbers show:—

Temperature.	Vapour density.
784°	31·77
796	31·36
815	31·00
928	29·00
968	27·30
985	27·00

The results show that in comparison with nitrogen dioxide, NO_2, which is completely decomposed below 620°, nitrosyl chloride is a highly stable compound.

Nitrosyl chloride in its reactions with water behaves as the chloride of nitrous acid, and inasmuch as nitrous acid not only forms nitroso-compounds, but also hydroximes by interaction with the CH_2 group. nitrous acid would appear to have the formula O:N·OH, and the chloride the formula O:N·Cl. As nitric oxide and nitrosyl chloride show no tendency to polymerise, the union which takes place between

NO_2 and NO_2 at temperatures below 140° is probably established between oxygen atoms, and as only like molecules of NO_2 are concerned in the formation of nitrogen peroxide, it is unlikely that the latter has an unsymmetrical formula : the formula O:N·O·O·N:O would appear to satisfy the requirements of the case; this leads to the formula O:N·O for the dioxide, and it may be that the instability of the dioxide is due to the unsaturated condition of the oxygen.

97. "The volumetric estimation of tellurium." By Dr. B. Brauner

Hitherto only gravimetric methods have been adopted in estimating tellurium, and as they involve the use of weighed filters, the determination is subject to considerable error, besides occupying much time. The author describes two volumetric processes. The first is based on the reduction of solutions of tellurium dioxide by stannous chloride :—

$$TeCl_4 + 2SnCl_2 = Te + 2SnCl_4,$$
$$TeO_2 + 2SnCl_2 + 4HCl = Te + 2SnCl_4 + 2H_2O.$$

The tellurium compound, together with muriatic acid, is digested with excess of stannous chloride, and the excess subsequently determined by iodine and thiosulphate.

The second method consists in adding an excess of potassium dichromate solution to the solution of tellurium dioxide in muriatic acid, the excess of dichromate being subsequently determined by means of ammonium ferrous sulphate :—

$$3TeO_2 + K_2Cr_2O_7 + 8HCl = 3TeO_3 + 2KCl + Cr_2Cl_6 + 4H_2O.$$

Results are quoted showing that the first method gives satisfactory results ; but the second does not appear to be one of practical value.

At the next meeting, on December 18th, the following papers will be read :—

"The constitution of dehydracetic acid." By Dr. Collie.

"The theory of dissociation into ions and its consequences." By S. U. Pickering.

"The α- and β-modifications of benzene hexachloride." By Dr. Matthews.

"The fermentation of calcium glycerate; an optically active glyceric acid." By Professor P. F. Frankland and W. Frew.

"Phenuvic acid." By Dr. Colefax.

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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 90. Session 1890–91.

December 18th, 1890. Dr. W. J. Russell, F.R.S., President, in the Chair.

Messrs. William J. Butcher, Thomas Platts, Charles T. Branson and Wm. H. Barraclough were formally admitted Fellows of the Society.

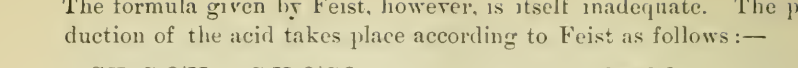
Certificates were read for the first time in favour of Messrs. Charles Norris Adams, M.A., 128, Chorlton Road, Manchester; Robert John Brown, 76, Grenville Street, Stockport; Frederick John Bloomer, 7, Boundaries Road, Balham, S.W.; Robert Bond Greaves, 154, Cemetery Road, Sheffield; Frederick William Harrold, 12, Hereford Gardens, Park Lane, W.; Edgar J. Millard, 50, Hillside Road, Stamford Hill, N.; Frederick Herbert Moore, 45, St. Mary's Road, Peckham, S.E.; Michael Samuel Bickering, 40, Price Street, Burslem, Stoke-on-Trent; William Jackson Pope, South Street, Ponders End; A. H. Tapp, The Gables, Shortlands, Kent.

The following papers were read:—

98. "Note on the constitution of dehydracetic acid." By Norman Collie, Ph.D., F.R.S.E.

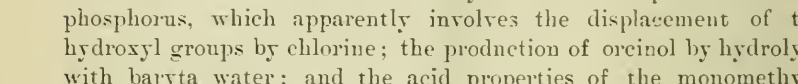
During the investigation of the effect of heat on ethylic β-amidocrotonate, the production of lutidone derivatives seemed to point to a close resemblance existing between the products formed from the crotonic salt and ethylic acetoacetate when heated. The author was, therefore, lead to enquire into the formulæ which various investigators had given to dehydracetic acid, the condensation product formed when ethylic acetoacetate is distilled. This peculiar acid has for long been the subject of investigation, and the various formulæ which have been suggested are all open to criticism, as Feist in his very excellent paper on this acid (*Annalen*, **257**, 253) has shown.

The formula given by Feist, however, is itself inadequate. The production of the acid takes place according to Feist as follows:—

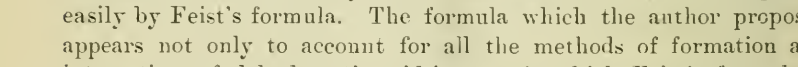


He discards the carboxylic group in his formula, as Ostwald has shown that the conductivity of the substance precludes the assumption that it is a true acid.

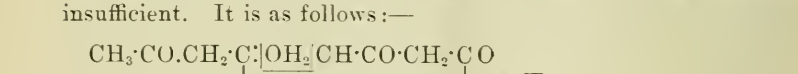
The formation of a dichloride by the action of pentachloride of phosphorus, which apparently involves the displacement of two hydroxyl groups by chlorine; the production of orcinol by hydrolysis with baryta water; and the acid properties of the monomethylic derivative noticed first by Perkin cannot, however, be interpreted easily by Feist's formula. The formula which the author proposed appears not only to account for all the methods of formation and interactions of dehydracetic acid in cases in which Feist's formula is satisfactory, but also in those in which Feist's formula is evidently insufficient. It is as follows:—



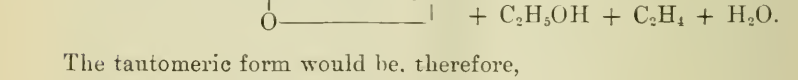
The tautomeric form would be, therefore,



The formation of a dichloride can easily be represented, also the existence of an acid monomethyl derivative; the formation of orcinol would take place as follows:—



when treated with baryta water would yield



Geuther, the discoverer of dehydracetic acid, first suggested, in 1866, that it was formed by the dehydration of acetic acid, $4CH_3COOH = C_8H_8O_4 + 4H_2O$. This idea is shown to be correct if we consider the synthesis of this acid by heating chloride of acetyl and pyridine,

$$CH_3{\cdot}CO\,\overline{|\,Cl\quad H\,|}\,CH_2CO\,\overline{|\,Cl\quad H\,|}\,CH_2{\cdot}CO\,\overline{Cl\quad H}\,CH_2COCl,$$

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}\underset{\underset{|}{O}}{C}{:}CH{\cdot}CO{\cdot}CH_2{\cdot}\underset{\underset{Cl}{|}}{C}O,$$
$$\qquad\qquad\qquad\quad\overline{|\,H\qquad\qquad}\;\overline{|}$$

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}\underset{\underset{|}{O}}{C}{:}CH{\cdot}CO{\cdot}CH_2{\cdot}\underset{\underset{|}{}}{C}O,$$
$$\qquad\qquad\qquad\quad\overline{\qquad\qquad\qquad}$$

and if we take acetoacetic acid as *diacetic acid*, the dehydracetic acid becomes the $\hat{c}$-lactone of tetracetic acid.

99. "The theory of dissociation into ions, and its consequences." By S. U. Pickering.

According to the present physical theory of solution, the only change which occurs when hydrogen chloride gas is dissolved in water is the dissociation of the HCl molecules into their ions: this change Arrhenius said must absorb heat, and, if so, there must have been creation of heat, as heat is, as a matter of fact, evolved during the dissolution. It appears that this difficulty is now met by supposing that the heat absorbed in the dissociation of the molecule into atoms is more than counterbalanced by the heat evolved in the combination of electrical charges with the atoms. This involves the idea of these charges being things independent of the atoms, and being called into existence from nowhere, and by no assignable means; it involves the idea of matter being capable of combining with energy, or an affection of matter, and thereby evolving heat; and it necessitates the conclusion that electrical charges of an opposite sign repel each other, and act antagonistically to chemical attraction. Such conceptions seem scarcely possible, and are in direct opposition to Faraday's electrochemical theory. Calling the ions "allotropic atoms" instead of "charged atoms" would seem to be merely a change of name, which obviates none of those objections.

The theory would, unlike the hydrate theory, appear to be incapable of giving any satisfactory explanation of the absorption of heat which occurs when many solid salts are dissolved in water. It may also be shown that the potential energy of a dissolved salt must be intermediate in many cases between that of the solid and gaseous salt, a fact which it is difficult to reconcile with the idea of the dissolved substance being in any sense in an atomic condition. In some cases, moreover, the thermal results attending the dilution of a dilute solution must lead to the conclusion that the formation of ions from the gaseous molecules absorbs heat, whereas in the same case the heat of dissolution of the ordinary gaseous salt is found to be a large positive quantity, and must lead to a diametrically opposite conclusion.

It must be noticed that the first hypothesis of Clausius—that a few molecules in solution are dissociated into their ions by accidental superheating—would seem to have little in common with the present dissociation theory. The second hypothesis of Clausius—that a free interchange of atoms can take place between molecules without necessarily resulting in the liberation of atoms—would, however, seem to be sufficient to explain all the facts of electrolysis, and it obviates the objections which may be raised against the idea of there being even a few free atoms in solution.

Discussion.

Professor Ramsay agreed with Mr. Pickering that many difficulties still remained to be solved before accepting the theories of Arrhenius and Van't Hoff in their entirety. He thought, however, that a theory, whatever its nature, could not be regarded as an absolute explanation of phenomena, but merely as a mental picture, whereby phenomena familiar to our senses could be conceived as analogous to those which do not directly appeal to our senses. It might well be possible that the analogy was a defective one; "we explain," many phenomena by the "atomic theory," but have a very limited conception of an "atom;" and the analogy between dilute solutions and gases must also be accepted merely as provisional—as a means of connecting together a great number of phenomena which would otherwise remain isolated facts. By all means let us draw attention to seeming discrepancies; to explain them may involve modification of the theory; but, until we have a better one, let us accept one which correlates a large number of phenomena which have not otherwise been united under any scheme.

Mr. Pickering said that he certainly could not agree with Professor Ramsay's contention that the dissociation theory should be received because it explained certain numerical relations, in spite of the fact, which Professor Ramsay appeared to admit, that it could not be supported on any rational grounds. He scarcely thought that Professor Ramsay could be right in saying that the dissociationists would attempt to explain some of the difficulties by stating that energy is a form of matter. If such were the case, all our present science must be wrong; and even though this view might account for heat (? matter or motion) being developed when this energy-matter combined with ordinary matter, we should still not be justified in calling it into existence from nowhere just when it suited our convenience. Professor Ramsay's suggestion that no molecules could react chemically would lead to the conclusion that no chemical change could occur unless the molecules were previously dissociated by heat or

some other external agency, a conclusion which would obviously be at variance with known facts.

Ostwald's experiment, in which a current produced by static electricity effects electrolysis, can certainly be explained on the dissociation theory, but so also it can, of course, on any other theory; it is difficult, therefore, to see how it can be brought forward by Ostwald as a conclusive proof of the dissociation theory.

100. "The fermentation of calcium glycerate by *Bacillus ethaceticus*." By Percy F. Frankland, Ph.D., and William Frew.

The authors describe the fermentative decomposition of calcium glycerate brought about by a micro-organism, previously isolated and described by one of them (*Proc. Roy. Soc.*, **46**, 345), and to which the name of *Bacillus ethaceticus* was given, in consequence of the products, ethyl alcohol and acetic acid, to which it gives rise in several fermentations already studied. The products obtained in this fermentation again were principally ethyl alcohol and acetic acid, together with smaller proportions of formic and succinic acids. In the case of each completed fermentation, there was also found a quantity of a fixed acid amounting to about one-half of the glyceric acid employed; this acid was insoluble in ether, and in other respects resembled glyceric acid. Lead salts were prepared from this residual acid, but these were of a basic character, and could not be obtained in a pure state, but in composition they approximated to basic lead glycerates. The nature of this residual acid is further discussed in the following communication. As regards the other above-mentioned products, the following quantities were obtained, in each case from 60 grams of calcium glycerate, $(C_3H_5O_4)_2Ca,2OH_2$:—

Fermentation.	Ethyl alcohol.	Acetic acid.	Formic acid.	Total volatile acid calculated as acetic acid.
I	1·711 gram	6·065 grams	1·067 gram	7·456 grams
II	(lost)	6·187 „	0·985 „	7·472 „
III	(0·71 gram)	(3·694 „)	(0·0806 „)	(3·799 „)
IV	1 299 „	7·00 „	0·132 „	7·198 „

About one-half of the fermented liquid was lost in Expt. III, so that no value attaches to the absolute amounts found, but the ratio of alcohol to acids remained undisturbed by the loss.

The proportion of alcohol to acetic acid in Fermentations III and IV, in which but little formic acid was produced, is respectively

Fermentation III.... Alcohol . Acetic acid :: 1 : 5·35
„ IV.... „ „ 1 : 5·54

This relationship corresponds approximately to 1 mol. of alcohol to 4 mols. of acetic acid :—

$$C_2H_5OH : 4(CH_3{\cdot}COOH) = 46 : 240 = 1 : 5{\cdot}2.$$

The authors provisionally suggest the following as the equation according to which the glyceric acid undergoes this decomposition :—

$$5C_3H_6O_4 = C_2H_6O + 4C_2H_4O_2 + OH_2 + 5CO_2 + 3H_2.$$

This equation not only indicates the molecular relationship between the alcohol and acetic acid formed, but is also fairly in accordance with the proportions of these substances obtained in the decomposition of a given weight of glyceric acid.

101. "An optically active glyceric acid." By Percy F. Frankland, Ph.D., and William Frew, University College, Dundee, St. Andrews University.

The residual non-volatile acid referred to in the previous note is shown to be of the two oppositely active forms of which, according to Van't Hoff's theory, ordinary inactive glyceric acid is composed. By repeating the experiments on a much larger scale, the authors have succeeded in obtaining the calcium salt in the form of beautiful, transparent and colourless, prismatic crystals, whilst ordinary calcium glycerate is only obtainable as an indistinctly crystalline, granular mass.

The specific rotation at 14·4° C. in a solution containing 10 grams salt in 100 c.c. was found to be $[\alpha]_D = -12{\cdot}09$. Great difficulty was encountered in obtaining the specific rotation of the acid, in consequence of the tendency to anhydride-formation during the evaporation of its solutions. By decomposing a quantity of the calcium salt, corresponding to 2 grams glyceric acid, with oxalic acid and filtering, a specific rotation at 12° C. in a solution containing 2 grams in 10 c.c. of $[\alpha]_D = +2{\cdot}14$, was obtained. Thus, whilst the acid itself is dextro-rotatory, its calcium and sodium salts are strongly lævorotary. The anhydride also is strongly lævorotary, for by heating some of the acid for six hours on the water-bath, and then taking up with water, a solution giving a rotation of $-3{\cdot}2°$ was obtained, although a large quantity of a white substance (doubtless the anhydride) remained undissolved, so that this rotation must have been due to a small quantity only of the anhydride which had passed into solution (ordinary glyceric anhydride is said to dissolve in 646·8 parts of boiling water), so that its lævorotation must be very powerful

indeed. On the other hand, it was found that by continued digestion with water on the water-bath of a solution of active glyceric acid containing anhydride, the rotation became more and more right-handed, obviously in consequence of the gradual hydration of the anhydride. Perfectly analogous observations were made by Wislicenus in his well known studies on paralactic acid, for whilst this acid also is dextrorotary, its salts and anhydride are lævorotary, the latter most powerfully so. The authors refer to experiments previously made by Lewkowitsch (*Ber.*, 1883, 2720) to obtain the active modifications of glyceric acid, in which the mould *Penicillium glaucum* was grown in solutions of ammonium glycerate, and these solutions were afterwards found to possess a left-handed rotation.

102. "The α- and β-modifications of benzene hexachloride." By F. E. Matthews, Ph.D.

The author finds that benzene is readily converted into hexachloride by passing chlorine into a dilute (1 per cent.) solution of sodium hydroxide having a layer of the hydrocarbon on its surface; the action takes place in the dark, and even at the temperature of a freezing mixture, the rate of formation of the chloride depending practically only on the rate at which the chlorine is passed in. Hexachloride is also formed in presence of water alone, but it would seem that there is an advantage in using alkali, the amount of uncrystallisable products being less when it is used.

The crude hexachloride is a mixture of about 70 per cent. of the α-with about 30 per cent. of the isomeric β-hexachloride described by Mennier and Schüpphaus. The author finds that the two modifications may be separated by steam distillation, the α-variety alone being volatile.

The pure α-hexachloride crystallises in characteristic fern leaf-like forms melting at 157°. The β-hexachloride forms small, very brilliant crystals, and sublimes without melting; it is much less soluble than the α-compound, but, nevertheless, it appears to be impossible to separate the two modifications of fractional crystallisation. Determinations by Raoult's method indicate that both α- and β-compounds are to be represented by the same molecular formula, $C_6H_6Cl_6$. Both yield 1 : 2 : 4-trichlorobenzene when submitted to the action of an alcoholic solution of potassium hydroxide, the β-compound being much less readily attacked.

The author finds that bromine also acts additively in presence of dilute akali, and that additive compounds of other derivatives of benzene, &c., may be obtained by slight modifications in the mode of working.

Discussion.

Dr. Armstrong thought that Dr. Matthews's observations were of special interest and value, not only as a contribution to our knowledge of the addition compounds of benzene, but especially in relation to the theory of the formation of chlorides by the action of chlorine. In his address to the B. A. Chemical Section in 1885, he had suggested that perhaps the "induction" observed by Bunsen and Roscoe in a mixture of chlorine and hydrogen is due to the occurrence of a change in which a something is produced which then promotes action between the two gases, it being assumed that the pure gases would not interact. Subsequently, in the discussion among the members of the Electrolysis Committee, he had suggested, in reference to Pringsheim's observations on the influence of moisture, that perhaps the initial change was one involving the production from water and chlorine of hypochlorous acid, which would account for the expansion noticed to occur by Pringsheim supposing a gaseous hydrate of chlorine to be affected ($OH_2{\cdot}Cl_2 = HCl + HClO$). From this point of view, he had been led to try the effect of moist mercuric oxide as a chlorine "carrier," and had found that it certainly promoted the action of chlorine and bromine. Dr. Matthews's observations appeared in like manner to show that hypochlorous acid played an important part in chlorination. With regard to the constitution of the two hexachlorides, the evidence that both were symmetrical appeared by no means conclusive; it was not at all improbable that in one two chlorine atoms were associated with the same carbon atom.

Mr. Cross said that the action of hypochlorous acid on benzene was deserving of much further study. With the object of investigating the phenose described by Carius, he had devoted considerable time to the investigation, but hitherto unsuccessfully.

Dr. Colemann drew attention to inositol, the hexhydroxy-compound corresponding to benzene hexachloride. Four modifications of this compound were now known, two of which were optically active. These facts pointed to geometric isomerism as an explanation of the differences in constitution.

Dr. Matthews thought that under the conditions under which the hexachlorides were formed in his experiments it was very unlikely that intramolecular change should take place, such as would be involved in the formation of a compound containing two chlorine atoms attached to one carbon atom. He also thought that, taking Jungfleisch's observations on the formation of chlorides of chlorobenzenes into account, it was improbable that either hexachloride had an unsymmetrical constitution.

103. "The molecular volumes of the saturated vapours of benzene and of its haloid derivatives." By Sydney Young, D.Sc.

The author has already shown (Trans., **55**, 486) that when the four monohaloid derivatives of benzene are compared together at their boiling points under any equal pressure, these boiling points, expressed on the absolute scale, and also the molecular volumes of the liquids, bear a constant ratio to each other, whatever the pressure.

These results are in agreement with Van der Waals's generalisation, according to which the above ratios should be constant at "corresponding" pressures, which in this case are equal pressures, since the critical pressures are equal.

The molecular volumes, in the liquid state, of benzene and fluorbenzene were found to bear an approximately constant ratio to each other at their boiling points under "corresponding" pressures.

Determinations have now been made of the molecular volumes of the saturated vapours of these compounds by the method recently described to the Society. The results obtained show that the molecular volumes of the saturated vapours of the five compounds bear an approximately constant ratio to each other at all "corresponding" pressures (these pressures being again equal in the case of the halogen derivatives).

Professor Orme Masson has recently pointed out (*Phil. Mag.*, November, 1890) that the molecular volumes of the haloid derivatives of similar hydrocarbons, at their boiling points under normal pressure, bear the same ratio to each other as those boiling points, expressed on the absolute scale. In a short paper in the same number of the *Phil. Mag.*, the author showed that Masson's law is really a special case of a more general one, which should be true if Van der Waals's generalisations were strictly accurate. This relation may be expressed as follows:—The molecular volumes of any two substances, both in the liquid state and as saturated vapour, at their boiling points under "corresponding" pressures *should* be directly proportional to their absolute critical temperatures, and inversely proportional to their critical pressures.

When the critical pressures are equal, as in the case of the halogen derivatives of benzene, and possibly also of some or all of the groups of compounds examined by Professor Masson, the relation becomes simply:—The molecular volumes, both of liquids and of saturated vapour, of any two nearly related substances whose critical pressures are equal, at their boiling points under equal pressure, are directly proportional to their absolute critical temperatures, and therefore to their (absolute) boiling points under any equal pressures. The author has already shown that this relation holds good approximately

for the liquid state, and proof is now afforded that the relation is also approximately true for the saturated vapours.

With regard to the saturated vapours, the above generalisation may be stated in the following way, which probably may be found useful:—The densities of the saturated vapours (compared with hydrogen or air) of different substances, at their boiling points under "corresponding" pressures bear the same ratio to their theoretical vapour densities. So far as benzene and its halogen derivatives are concerned, this relation is found to hold good approximately within wide limits of pressure.

104. "Phenuvic acid." By A. Colefax, B.A., Ph.D.

The author has compared Schloesser's phenuvic acid with the phenylmethylfurfurancarboxylic acid of Paal, the work having been carried out at the suggestion of Professor Fittig; he finds that the two acids are isomeric. He discusses the constitution of the acids, and arrives at the conclusion that at present the evidence is insufficient to enable any decision to be arrived at.

105. "The action of phosphoryl trichloride on phosphorus pentoxide." By G. N. Huntly, Associate of the Normal School of Science.

In 1871, Gustavson noticed that after prolonged heating at 200° phosphoryl trichloride and phosphorus pentoxide interacted to form an apparently homogeneous mass. A similar product having recently been obtained by the action of chlorine on phosphorous oxide (Thorpe and Tutton, Trans., 1890, p. 572), at the suggestion of Professor Thorpe the author repeated Gustavson's experiments. The behaviour of the substance obtained towards neutral solvents and on distillation leads to the conclusions:—

(1.) That there is no evidence that any compound of the composition PO_2Cl or $(PO_2{\cdot}Cl)_n$ exists.

(2.) That the interaction of phosphoryl trichloride and phosphorus pentoxide is not represented by the equation $P_2O_5 + POCl_3 = 3PO_2Cl$, but is much more complex.

(3.) That pyrophosphoryl chloride, $P_2O_3Cl_4$, and a substance containing chlorine and phosphorus in the ratio of 5P : 7Cl are produced in the interaction.

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PROCEEDINGS

OF

THE CHEMICAL SOCIETY.

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JANUARY—DECEMBER, 1891.

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DATES OF ISSUE OF THE MONTHLY NUMBERS OF THE JOURNAL OF THE CHEMICAL SOCIETY TO FELLOWS.

January number	was issued	19th January.
February	,,	4th February.
March	,,	6th March.
April	,,	2nd April.
May	,,	30th April.
June	,,	9th June.
July	,,	8th July.
August	,,	1st August.
September	,,	1st September.
October	,,	2nd October.
November	,,	7th November.
December	,,	10th December.
Index	,,	will be issued in January.

LIST OF GRANTS MADE FROM THE RESEARCH FUND DURING THE YEAR.

£75 to Professor W. H. Perkin, Jun., for the further investigation of closed carbon chains.

£10 to Mr. A. E. Tutton for the crystallographic investigation of double sulphates of rubidium and cæsium and metals of the magnesium group.

£10 to Mr. Sudborough for the study of the action of nitrosyl chloride on unsaturated hydrocarbons.

£5 to Dr. Cook for the study of the decomposition of bromates and iodates by heat.

£15 to Mr. W. Sinclair for the study of tetramethylene ketones.

£10 to Mr. J. Stenhouse for the study of trimethylene derivatives.

£10 to Mr. G. Young for the study of derivatives of pentanetetracarboxylic acid.

£25 to Professor Munro for the further study of nitrification.

£10 to Mr. G. H. Robertson for the study of the electrolytic reduction of lead sulphate.

£10 to Dr. Ruhemann for the continuation of an investigation of mucic acid.

£10 to Mr. A. R. Ling for the study of halogen derivatives of quinone.

£15 to Dr. J. Walker for the investigation of the composition of the vapours given off by mixed liquids.

£5 to Dr. Laycock for an examination of the products of the dry distillation of bran with lime.

£10 to Dr. J. Leicester for the further study of the action of orthodiamines on quinones.

£10 to Messrs. Linder and Picton for an investigation of the different grades of solution.

£25 to Messrs. Cross and Bevan for the continuation of their studies of cellulose.

£50 to Professor Smithells towards the payment of an assistant for further experiments on the chemistry of flames.

£15 to Mr. Wynne for the study of the quinolinesulphonic acids.

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Name.	Proposed.	Elected.
Adams, Charles N.	December 18th, 1890	February 19th.
Alger, Harold	November 5th	December 3rd.
Allen, George J.	,, ,,	,, ,,
Appleton, Henry A.	January 15th	February 19th.
Ashcroft, George A.	November 5th	December 3rd.
Aydans, Charles A.	January 15th	February 19th.
Bairston, John	November 5th	December 3rd.
Baly, Charles C.	,, ,,	,, ,,
Barnes, Edward A.	March 19th	May 7th.
Barrett, J. Treeby	November 5th	December 3rd.
Bate, William	March 5th	May 7th.
Bater, Claude H.	February 19th	,, ,,
Beadle, Clayton	January 15th	February 19th.
Belbin, T. St. J.	April 2nd	June 18th.
Bell, Albert E.	February 5th	May 7th.
Berry, Thomas W.	November 5th	December 3rd.
Bloomer, John F.	December 18th, 1890	February 19th.
Bovell, John R.	November 5th	December 3rd.
Brown, Edward	May 7th	June 18th.
Brown, Robert J.	December 18th, 1890	February 19th.
Burford, Samuel F.	November 5th	December 3rd.
Byrne, Thomas	January 15th	February 19th.
Calder, William A. S.	June 4th	December 3rd.
Charles, Rhys P.	February 5th	May 7th.
Chorley, John C.	November 5th	December 3rd.
Cole, Arthur	January 15th	February 19th.
Colefax, Arthur	November 20th, 1890	,, ,,
Congdon, Ernest A.	May 7th	June 18th.
Cooper, Walter J.	February 19th	May 7th.
Corbett, Charles H.	December 4th, 1890.	February 19th.
Cory, George W.	November 5th	December 3rd.
Darling, Thomas	November 5th	,, ,,
Donovan, Hendrie T.	December 4th, 1890 .	February 19th.
Dreaper, W. Porter	May 7th	June 18th.
Duncan, William	April 16th	,, ,,
Eastwick, Charles E.	November 5th	December 3rd.
Elford, Percy	,, ,,	,, ,,
Evans, Frederick A.	March 19th	May 7th.
Fowler, Gilbert J.	February 5th	,, ,,
Fitze, Joseph	March 19th	,, ,,
Foster, John A.	,, ,,	,, ,,
Fulcher, Lionel W.	November 5th	December 3rd.
German, George, Jun.	,, ,,	,, ,,
Gibbins, Berington H.	February 5th	May 7th.
Greaves, Robert B.	December 18th, 1890	February 19th.
Gregory, Alfred J.	April 16th	June 18th.

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Hall, Alfred D.	November 5th	December 3rd.
Hall, Archibald	„ „	„ „
Harrold, Frederick W.	December 18th, 1890	February 19th.
Hart, William B.	February 5th.	May 7th.
Heath, John W.	June 4th.	December 3rd.
Hiepe, William L.	February 19th	May 7th.
Holliday, John	November 5th	December 3rd.
Holloman, Frederick R.	May 21st	June 18th.
Hooper, Ernest F.	November 20th, 1890	February 19th.
Jenkins, Henry C.	December 4th, 1890.	„ „
Jones, Moses W.	November 20th, 1890	„ „
Joseland, Walter H.	March 19th	May 7th.
Kipping, F. Stanley	February 19th	„ „
Knowles, John.	April 16th	June 18th.
Langham, Edgar N.	February 5th	May 7th.
Lauder, Alexander	March 5th	„ „
Leather, John W.	November 5th	December 3rd.
Leeds, Frank H.	April 16th	June 18th.
Leffler, Rudolf L.	June 4th.	December 3rd.
Leicester James	February 5th	May 7th.
Lennox, Robert	June 4th	December 3rd.
Ludlow, Lionel	November 5th	„ „
Macdonald. William	February 5th	May 7th.
Macfie, Robert A. S.	April 16th	June 18th.
Marshall, John W.	November 5th.	December 3rd.
Marshall, Reginald L.	January 15th.	February 19th.
Martin, William M.	December 4th, 1890.	„ „
McLaren, Daniel.	November 5th	December 3rd.
Merrils, Frederick J.	February 5th	May 7th.
Michael. Arthur	May 21st	June 18th.
Millard, Edgar J.	December 18th, 1890	February 19th.
Mitchell, Charles A.	February 19th	May 7th.
Mitchell, Thomas	May 7th	June 18th.
Moore, Frederick H.	December 18th, 1890	February 19th.
Morris, Joseph	November 5th	December 3rd.
Morrison, George R.	February 5th	May 7th.
Mousley, Harry J. M.	May 7th	June 18th.
Naylor, William	November 5th	December 3rd.
Neilson, Thomas	„ „	„ „
Newlands, William P. R.	June 18th.	„ „
Notter, James L.	April 2nd	June 18th.
Ough, Lewis.	February 5th	May 7th.
Oxford, Arnold W.	December 4th, 1890.	February 19th.
Perkin, F. M.	May 21st	June 18th.
Pickering. Michael S.	December 18th, 1890	February 19th.
Pope, William J.	„ „ „	„ „
Priestley, Laurence.	June 18th.	December 3rd.
Randall, Percy M.	February 19th	May 7th.
Rhodes, Edward	May 7th	June 18th.

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Rose, Tom K.	January 15th	February 19th.
Rossiter, Edmund C.	May 21st	June 18th.
Sauyal Abhayacharan.	November 5th	December 3rd.
Scott, Charles K.	June 4th.	„ „
Searl, Albert	February 5th	May 7th.
Shaw, Herbert D.	December 4th, 1890.	February 19th.
Shields, John.	May 21st	June 18th.
Smith, R. Greig	January 15th	February 19th.
Solomon, Frank O.	April 16th.	June 18th.
Stephenson, Thomas.	June 4th	December 3rd.
Stockdale, R.	December 4th, 1890.	February 19th.
Storey, James A.	February 5th	May 7th.
Sucre, Howard C.	January 15th	February 19th.
Sykes, Matthew C.	„ „	„ „
Symes, Kenelm E.	December 4th, 1890 .	„ „
Tapp, A. H.	December 19th, 1890	„ „
Taylor, John	May 7th	June 18th.
Tetley, Frederick	April 2nd	„ „
Thonger, Cecil G. F.	March 5th.	May 7th.
Thorp, Walter.	November 5th	December 3rd.
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Velling, Frederick W. de.	December 4th, 1890.	February 19th.
Ward, Thomas A.	June 18th.	December 3rd.
Weber, Otto C.	April 16th	June 18th.
Wellington, Stephen N.	November 20th, 1890	February 19th.
White, Henry	June 4th.	December 3rd.
Wild, John	March 19th.	May 7th.
Wilkinson, David	November 20th, 1890	February 19th.
Will, Dr. W.	January 15th	„ „
Williams, Seward W	April 16th	June 18th.
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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 91. Session 1890–91.

January 15th 1891. Dr. W. J. Russell, F.R.S., in the Chair.

Certificates were read for the first time in favour of Messrs. Henry Austin Appleton, 19, South Street, Middlesbro'; John Charles Aydans, 44, Crescent Road, Plumstead, S.E.; Clayton Beadle, Beadonwell, Belvedere, Kent; Thomas Byrne, Glenville, Dundrum, co. Dublin; Arthur Cole, B.A., Holmleigh, Charles Street, Berkhamsted; Reginald Lorn Marshall, 25, Lancaster Park, Richmond; Tom Kirke Rose, 9, Royal Mint, E.; R. Greig Smith, Springwells, New Street, Musselburgh; Howard C. Sucré, Breeze House, Higher Broughton, Manchester; Matthew Carrington Sykes, Sykeshurst, Barnsley, Yorks; W. Will, Ph.D., 1, Beethoven Strasse, Berlin, N.W.

The following papers were read:—

1. "Magnetic rotation." By W. Ostwald.

The magnetic rotation of organic compounds, according to Perkin, is an additive function of their composition and equal to the sum of the rotations of the components, but this is not the case with the rotation of inorganic compounds, which is usually found greater than that calculated on such an assumption. In the case of hydrogen chloride, for instance, the calculated value is about 2·18, and as a matter of fact the value obtained for hydrogen chloride dissolved in an organic solvent, isoamyl oxide, is 2·24, but when disolved in water the value found is from 4·05 to 4·42, increasing with the dilution. The author points out that these exceptional values are only obtained in the case of electrolytes, and that they must therefore be referred to a fundamental difference existing between the constitution of electrolytes and that of non-conductors. That such a difference exists has been already deduced from other considerations, and has led Arrhenius

to the formulation of the theory of electrolytic dissociation. The author claims that the facts established with regard to magnetic rotation are in perfect accordance with this theory, and that any exceptional values in the magnetic rotations of electrolytes are due to the occurrence of electrolytic dissociation.

Discussion.

Mr. Pickering said that in Professor Ostwald's attempt to appropriate Dr. Perkin's results on the magnetic rotation of solutions of electrolytes in support of the dissociation theory, no attempt was made to explain what connection should exist between the magnetic rotation and the supposed dissociation into ions, but it was boldly stated that if, as in the case of hydrogen chloride, the magnetic rotation and dissociation both increased with dilution, the result proved the truth of the dissociation theory, while equal support to this latter theory was afforded if, as in the case of sulphuric acid, dilution diminished the rotation and increased the dissociation; and the most astonishing part of the argument appeared to be that the nearly double magnetic rotations obtained in some cases should be brought forward as a proof of dissociation, when the observations were made on solutions so strong that the dissociation theory represents them as containing hardly any dissociated substance at all. Surely the natural conclusion to draw from such a doubling when it occurs in the absence of dissociation would be that it could not be explained by dissociation.

2. "The vapour density of ammonium chloride." By Frank Pullinger, B.A., B.Sc., and J. A. Gardner, B.A.

The authors have made experiments at various temperatures on the vapour density of ammonium chloride. The apparatus used was that of Victor Meyer. In view of the well-known results of Wurtz concerning the vapour density of phosphorus pentachloride, it was decided to vaporise the ammonium chloride into an atmosphere of ammonia—one of the products of dissociation. In the first instance the experiments were conducted at a moderate red heat and the salt was vaporised into air. The mean result of five experiments was 0·926; the calculated value for complete dissociation is 0·921.

At 1040° C. (the temperature of boiling zinc), Deville and Troost, using Dumas' method, found the vapour density to be 1·000.

Boiling sulphur was next used, giving a temperature of 448° C. The salt was first vaporised into air. The values found were 0·983 and 0·932. The air was then displaced by ammonia, and the values obtained were 0·939, 0·994 and 1·009.

At a temperature of 360° C. (that of boiling anthracene), the relative density in an atmosphere of air was 0·944, while in an atmosphere of ammonia it was 1·128 and 1·141.

It is evident that in this latter case the ammonium chloride was not wholly dissociated.

It was found impossible to vaporise the salt into ammonia at 300° C. in a bath of boiling α-naphthylamine. In one case, 0·0175 gram of ammonium chloride was heated for 40 minutes, but the loss in weight during that time was only 0·0045 gram, and the volume of ammonia expelled from the apparatus was only 0·91 c.c. In another experiment, 0·0037 gram was taken, and the loss during 40 minutes was 0·0021 gram, no gas being expelled. The vaporisation into air, however, goes on with comparative rapidity at this temperature, and the values found were 0·982, 0·986 and 0·985. The time taken for expulsion of the air was 10—12 minutes.

At a temperature of 354° C., Deville and Troost, using a bath of mercury vapour, found that the vapour density was 1·01. The authors propose to continue their experiments at temperatures between 300° and 360°.

3. "Chlorinated phenylhydrazines." By J. T. Hewitt, B.A., B.Sc.

The author describes the following compounds:—

Orthochlorophenylhydrazine, $ClC_6H_4{\cdot}NH{\cdot}NH_2$, and its hydrochloride.
Orthochlorophenylsemicarbazide, $ClC_6H_4{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2$.
Orthochlorophenylphenylsemithiocarbazide, $ClC_6H_4{\cdot}N_2H_2{\cdot}CS{\cdot}NHPh$.
Orthochlorophenylhydrazinepyruvic acid, $ClC_6H_4{\cdot}N_2H_2{\cdot}CMe{\cdot}CO_2H$.
Parachlorophenylphenylsemithiocarbazide.
Formylparachlorophenylhydrazine, $ClC_6H_4{\cdot}NH{\cdot}NH{\cdot}COH$.
Parachlorophenylhydrazine parabanate, $C_3O_3N_2H_2{\cdot}2C_6H_7N_2Cl{\cdot}OH_2$.
Diparachlorophenylurea, $CO(NH{\cdot}C_6H_4Cl)_2$.

The compounds formed by interaction of aldehydes or ketones and orthochlorophenylhydrazine, according to the author, are very unstable.

4. "A new modification of phosphorus." By H. M. Vernon, Scholar of Merton College, Oxford.

Observations on the rate of rise of temperature of phosphorus and other experiments have led the author to the conclusion that one or other of two different modifications of phosphorus may result when fused phosphorus solidifies; the new variety is formed when the phosphorus is cooled below its solidifying point and then solidified, and has an undefined melting point; the ordinary variety of well-

defined melting point being formed when solidification of the phosphorus sets in directly the point of solidification is reached without the temperature sinking below this point. From examination of crystals under the microscope, the author considers that the new variety crystallises in rhombic prisms, the ordinary crystallising in octahedra; he summarises the properties of the two modifications in the following table:—

Octahedral variety.	*Rhombic variety.*
Has a definite melting point at 44·3°.	Has no well defined melting point; melts at about 45·3°.
Relative density at 13°, 1·8177. Has a considerably greater latent heat of fusion than rhombic variety.	Relative density at 13°, 1·8272.
Solidifying point 43·8°.	Solidifying point 43·8°.

Discussion.

Mr. Pickering thought that Mr. Vernon's conclusions must be accepted at present with great reserve. A difference of 1° in the melting points, especially where one of these melting points was undefined, might easily be accounted for by the presence of dissolved matter, accidental impurity, products of oxidation, or some of the oil used to cover the molten phosphorus. Mr. Vernon's curves seem to prove conclusively that this was the case, for that portion which represented the temperature of the substance while it was melting was very much curved, instead of being horizontal as it would be if the phosphorus had been pure. The small difference in the densities —0·01—was equally unsatisfactory, and even if any conclusion could be drawn from a superficial examination of the crystals under the microscope, it would be invalidated by the fact that the specimens examined had both been dissolved in, and recrystallised from, benzene, for, since fusion had been shown to render the two supposed varieties identical, it was more than probable that dissolution would do the same. It was noticeable that although the two modifications were supposed to be obtained by cooling fused phosphorus, yet the fused phosphorus solidified in each case at the same temperature, a temperature which was not identical with the melting points of either of the supposed varieties.

Mr. Tutton concurred with Mr. Pickering in considering that such an important conclusion as to the existence of a new variety of phosphorus was not justified by the data brought forward. It is well known that phosphorus is a substance which exhibits the property of superfusion in a high degree, and the thermal disturbance caused by the sudden solidification of a superfused mass would be likely to influence the results of a determination of melting point made after

solidification under such circumstances. In the speaker's own experiments on the fusion of phosphorous oxide, which also exhibits superfusion in a very marked manner, a determination of melting point after such solidification from a state of superfusion frequently yielded values differing sometimes by a whole degree from the true melting point of the substance. It is not at all surprising that a difference of a degree should have been observed by Mr. Vernon, but this fact in itself could scarcely be said to furnish proof of the existence of two modifications. The speaker also took exception to the arbitrary manner in which, from a microscopical examination of which absolutely no details are given, it was concluded that the supposed new modification crystallised in rhombic prisms. Remembering that many really isotropic substances frequently exhibit polarisation colours, owing to their deposition probably in a slight state of strain, it would not be surprising if regular crystals of phosphorus were to exhibit polarisation. It is certainly necessary to have, at least, data concerning the mode of extinction of the crystals and their behaviour in convergent light before any conclusion can be arrived at as regards their crystalline system.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE NEXT BALLOT.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

Aydans, John Charles,

44, Crescent Road, Plumstead, S.E.

Manager, Explosives Branch, Royal Laboratory, Royal Arsenal, Woolwich. *As Student.*—First Advanced Certificates (S. & A. Dept.) for Theoretical and Practical Inorganic Chemistry. Certificates in Organic, Theoretical and Practical, and in Physics. *As Teacher.*—Several years Assistant in Practical Chemistry at the Science Department Classes, Royal Arsenal, Woolwich. About 20 years' experience in the manipulation of material, and its behaviour in the production of explosive war and pyrotechnical stores, under the War Department, Woolwich Arsenal.

F. A. Abel. W. Kellner. W. H. Deering.
W. Y. Dent. G. Smith.

Appleton, Henry Austin,

19, South Street, Middlesbro'.

Analytical Chemist. Four years with Dr. James Baynes, of Hull: one year Chemist to the Hull Oil Manufacturing Company, Limited, Stoneferry.

Jas. Baynes. M. D. Penney. Geo. A. Milne.
John S. Linford. *R. H. Harland.*

Adams, Charles Norrish, M.A.,

128, Chorlton Road, Manchester.

Science Master at The Hulme Grammar School, Alexandra Park, Manchester. 1st Class Natural Sciences Tripos, Cambridge, Part I. 1884. 2nd Class Natural Sciences Tripos, Cambridge, Part II. 1886. Foundation Scholar of Christ's Coll., Cambridge, in Chemistry. Have worked at Chemistry at Exeter School from 1877 to 1882, and in Cambridge Univ. Laboratory from 1882—86. Since then engaged in teaching that subject. Have done original work on "Time

Reactions" and on "Electrolytic Resistance with Regard to Hydration of the Dissolved Salt."

Harold B. Dixon. William Thomson.
W. W. Haldene Gee. Francis Jones.
W. A. Shenstone.

Bloomer, John Frederick,

7, Boundaries Road, Balham, S.W.

Assistant Chemist to Brin's Oxygen Co. Three years student in Chemistry at the Science and Art Institute, Walsall. Three years Assistant to the Professor of Chemistry, University College of Wales, Aberystwyth. Two and a half years Assistant Chemist to Brin's Oxygen Co.

Leonard Temple Thorne. John Heron.
C. W. Stephens. John Cuthbert Welch.
Alfred J. Shilton. H. Lloyd Snape.
Thomas Turner.

Beadle, Clayton,

Beadonwell, Belvedere, Kent.

Chemist to William Joynson and Son, St. Mary Cray. Three years in the laboratory of Messrs. Cross and Bevan as pupil and assistant. Special work—investigations upon Plant Fibres: preparation of Reports upon Colonial and Indian exhibits of Fibres, C.I.E. 1886. General chemical experience.

C. W. Heaton. Chas. Fred. Cross.
W. J. Dibdin. Edward Bevan.
Leonard Temple Thorne.

Brown, Robert John,

76, Grenville Street, Stockport.

Lecturer on Chemistry. Master of Science of Victoria University (Honours in Chemistry). Former student of Chemistry in the Universities of Heidelberg and Berlin. At present Principal and Lecturer in Chemistry in the Stockport Technical School.

Walter Myles Gardner. G. H. Bailey.
J. B. Cohen. Arthur Harden. Harold B. Dixon.

Byrne, Thomas,

Glenville, Dundrum, co. Dublin.

Student of Chemistry. Associate of the Royal College of Science for Ireland, in the Faculty of Manufactures.

W. N Hartley. T. A. Shegog.
W. E. Adeney. Clement J. Leaper.
Richard J. Moss.

Cole, Arthur, B.A.,

Holmleigh, Charles Street, Berkhamsted.

Lecturer on Chemistry and Physics at King Edward VI Grammar School, Berkhamsted. First Class in Natural Sciences Tripos, Part 1; B.A. of Cambridge University, and Prizeman of Christ's College.

S. Ruhemann. Sidney Skinner. T. H. Easterfield.
H. J. H. Fenton. *M. M. Pattison Muir.*

Colefax, Arthur, B.A., Ph.D.,

Ashgrove, Bradford, Yorkshire.

Late Natural Science Postmaster, Merton College, Oxford. Studied in Oxford under Professor Odling, graduated B.A., First Class Honours Chemistry. Studied in Germany under Professor Fittig. Graduated Ph.D. at Strassburg.

William Odling.	John Watts.	W. W. Fisher.
V. H. Veley.	T. A. Lawson.	J. E. Marsh.
William Esson.	R. J. Friswell.	*H. B. Baker.*

Corbett, Charles Henry,

Barnard Castle.

Science Teacher and Schoolmaster (1st Division). Studied under the late Mr. T. Eltoft, F.C.S., of St. Bartholomew's Hospital. Student of Chemistry twelve years. First Class Qualifications under Science and Art Department. Attended Summer Course of Lectures in Chemistry, and Laboratory Practice for Science Teachers under Prof. Japp, Ph.D., Normal School of Science Qualified to teach fifteen subjects under the Science and Art Department. Science Lecturer for eight years at Barnard Castle and Middleton Centres. Just appointed Chemical Lecturer. I wish to take advantage of the Transactions, Library, &c., to assist in lectures on Chemistry.

Henry Stoker.	E. D. Walrond.	F. R. Japp.
W. Tate.	*John J. Pilley.*	*John Howard.*
E. J. Cox.	*Isaac S. Scarf.*	*G. H. Bailey.*
	W. Hibbert.	

Donovan, Hendrie Thomas,

Crumpton Street, Bridgetown, Barbados.

Analytical Chemist. Studied Chemistry at the Government Laboratory, Barbados, and at present Analyst to the Reef Manure and Chemical Works, Barbados.

W. H. Cannon. William Newton. Peter Coulson Bunn.
Frank L. Teed. *Matthew Cannon.*

Greaves, Robert Bond,

154, Cemetery Road, Sheffield.

Chemist (Pharmaceutical). Examinations of the Pharmaceutical Soc. Gt. Brit. and Sc. and Art Dept., S. Kensington. Member of the Pharmaceutical Society.

Henry J. Hardy. Charles Bradshaw. Wm. Ward.
G. T. W. Newsholme. *L. T. O'Shea.* *J. O. Arnold.*

Hooper, Ernest F.,

"Elmleigh," Beckenham.

Superintending Analytical Chemist to Messrs. Burt, Boulton, and Haywood's Chemical Works, Silvertown. Matriculated Student at the City and Guilds of Lond. Inst., S. Kensington, for over two years.

C. W. Heaton. Henry E. Armstrong. Alfred C. Young.
Herbert E. Kirby. *Walter A. Voss.*

Harrold, Frederick William,

12, Hereford Gardens, Park Lane, W.

Chief Assayer to the Goldsmiths' Company. Associate of the Royal School of Mines (Metallurgical Division).

W. C. Roberts-Austen. Alfred Gordon Salamon.
Frederic Jas. M. Page. Ed. Dillon.
F. W. Bayley. *Arnold Philip.*

Jones, Moses William,

343, Aspen Terrace, Church, Lancashire.

Analyst in Chemical Works. I have studied chemistry during the last eight years, and have been pupil and afterwards Assistant for three and a half years to Messrs. Crace-Calvert and Thomson, Analysts and Consulting Chemists, Royal Institution Laboratory, Manchester. Chemist to Messrs. Wm. Blythe & Co., Holland Bank, Chemical Works, Church, Lancashire.

William Thomson. A. B. Griffiths. Arthur Harden.
Thomas Fairley. Alfred H. Allen. *G. H. Bailey.*
J. B. Cohen.

Jenkins, Henry Charles,

Lorne Villa, Iverson Road, Hampstead, N.W.

Metallurgical Chemist, Associate and Bessemer Medallist of the Royal School of Mines. Received chemical training at Finsbury Technical College, and subsequently at the Royal College. Has since 1888 been engaged in conducting chemical researches.

W. C. Roberts-Austen. F. W. Bayly. Edwin J. Ball.
Bennett H. Brough. T. E. Thorpe. Alfred E. Tutton.

Moore, Frederick Herbert,

45, St. Mary's Road, Peckham, S.E.

For twelve years Assistant to Mr. G. H. Ogston, F.I.C., F.C.S., &c. Employed during that time in every variety of Chemical Analysis.

G. H. Ogston. Bernard Dyer. Otto Hehner.
William Newton. W. H. Cannon. *F. H. Perry Coste.*
P. Coulson Bunn.

Marshall, Reginald Tom,

25, Lancaster Park, Richmond, Surrey.

Analytical Chemist. Two years pupil and pupil assistant at Messrs. Cannon and Newton's Laboratory, 18 and 19, Fenchurch Street, E.C.

P. Coulson Bunn. W. H. Cannon. William Newton.
C. Heinrich Trinks. Frank L. Teed.

Millard, Edgar J.,

50, Hillside Road, Stamford Hill, N.

Manager of the laboratory of Messrs. C. J. Hewlett and Son, Charlotte Street, E.C., Manufacturing Pharmaceutical Chemists. Have attended two courses of Professor Redwood's lectures and two courses of Professor Dunstan's lectures on Chemistry at the Pharml. Society. Have passed both "minor" and "major" examinations of the Pharmaceutical Society. Have been five years analytical assistant to Charles Ekin, F.I.C., F.C.S. Author of papers on "Water Analysis," *Pharm. J.* [3], **18**, 917—998; "The Molybdate Test for Hypophosphites," *ibid.*, **19**, 585, Abstr., 1889, 548; "Examination of the Cream of Tartar Fruit from Pretoria," *Pharm. J.*, **20**, 829, &c.

M. Foster. M. Carteighe. Charles Ekin.
Wyndham R. Dunstan. T. Redwood. Thos. P. Blunt.
Robert H. Davies. *W. H. Symons.* *George S. Taylor.*
A. W. Gerrard. *Francis Ransom.* *Samuel Gale.*

Martin, William Morley,

Cardrew, Redruth.

Pharmaceutical Chemist (by Examination). Student in Mineralogy and Chemistry for five years at the Redruth and Camborne Laboratories.

John Woodland. J. J. Beringer. Jos. F. Burnett.
T. A. Ellwood. W. W. Fisher. *Thos. P. Blunt.*
Herbert W. Seeley. *E. E. Burnett.* *Arthur Turner.*
Cornelius Beringer.

Oxford, Arnold Whitaker,

8, Henrietta Street, Cavendish Square, London, W.

Vicar of St. Luke's Berwick Street, W. M.A. of Christ Church, Oxford. Student at Charing Cross Hospital in the Chemical Laboratory.

C. W. Heaton. Percy A. E. Richards. John Woodland.
S. Arch. Vasey. *T. A. Ellwood.*

Pickering, Michael Samuel,

40, Price Street, Burslem, Stoke-on-Trent.

Science Master at the Wedgwood Institute, Burslem. First Class Honours, Theoretical and Practical Inorganic Chemistry with Science and Art Department Bronze Medal, and Practical Organic Chemistry. Second Class Honours, Theoretical Organic Chemistry. Second Class Honours, in Chemistry, Intermediate Science Examination, London University. Six years' work in Chemical Laboratory. Two years' experience in teaching Chemistry. In charge of the Chemical Laboratory, Wedgwood Institute, Burslem.

Charles M. Stuart. A. Humboldt Sexton.
Sydney J. Harris, M.Sc. (Victoria). *E. J. Cox.*
James Spencer, B.Sc. (Lond.)

Pope, William Jackson,

South Street, Ponder's End.

Lecture Assistant in Chemical Department of the Central Institution, South Kensington. Spent two years at the Finsbury Technical College and three years at the Central Institution.

Henry E. Armstrong. W. P. Wynne. Gerald T. Moody.
Henry A. Miers. Holland Crompton.

Rose, Tom Kirke,

9, Royal Mint, E.

Assistant Assayer to the Royal Mint. Associate of the Royal School of Mines. Chemist to the Newbery-Vautin Gold Extrn. Co., 1888—90.

W. C. Roberts-Austen. Edwin J. Ball. F. W. Bayly.
E. Frankland. Bennett H. Brough.

Stockdale, R.,

The Grammar School, Leeds.

Science Master in above school. Obtained 2nd Class in Chemistry in Final Honour School of Nat. Sci. For two years Assistant Demonstrator in Oxford University Laboratory. Joint author of paper on "Camphor," in Trans., November, 1890.

William Odling. V. H. Veley. W. W. Fisher.
J. E. Marsh. John Watts. *Herbert McLeod.*

Sykes, Matthew Carrington,

Sykeshurst, Barnsley, Yorks.

D.P.H. Lond., L.R.C.P. Lond., M.R.C.S. Eng., L.S.A. Lond. Associate of State Medicine, London. Member of the Sanitary Institute, London.

Richd. Reynolds. F. W. Branson. William McCowan.
John Wm. Biggart. *J. Farrow Ballard.*

Shaw, Herbert D.,

Castle Mount, Sandal, nr. Wakefield.

Analytical Chemist. Full College course when Student. Four years analyst in dyeworks.

James Sharp. Thorp Whitaker. Arthur Stanley.
Watson Smith *William Thomson.*

Smith, R. Greig,

Springwells, New Street, Musselburgh.

Chemist. Bachelor of Science (Physical Experimental Sciences) of Edinburgh University. Assistant Professor of Chemistry in the Royal (Dick) Veterinary College.

Alex. Crum Brown. Leonard Dobbin. James Walker.
George Beilby. *W. H. Perkin, jun.*

Symes, Kenelm Edward,

Magdalen House, Bridport, Dorset.

Chemist and Brewer. Special Student in the Chemical Department of the Central Institution, City and Guilds of London Institute, during the Sessions 1889—90.

Henry E. Armstrong. W. P. Wynne.
Gerald T. Moody. Hugh Gordon. H. Crompton.

Sucré, Howard C.,

Breeze House, Higher Broughton, Manchester.

Manager and Secretary of Chemical Works. Student of Practical Chemistry for 10 years. Four years with Messrs. Hutchinson and Co., of Widnes; two to three years of this period as Sub-Manager. At present Manager and Secretary of Grimshaw Bros., Limited, Clayton, Manchester.

Harry Grimshaw. J. Carter Bell. Jno. J. Hickey.
Watson Smith. *Arthur F. Morgan.* *Thos. Tyrer.*

Tapp, A. H.,

The Gables, Shortlands, Kent.

Metallurgical Engineer. Studied at Cambridge University and

afterwards Metallurgy at the Royal Saxon School of Mines, Freiberg, Germany. Has been working two years in a chemical works.

H. J. H. Fenton. M. M. Pattison Muir.
Rudolph Messel. *A. H. Church.* *Alex. Muirhead.*

De Velling, Frederick William, B.A.,

High Street, Heckmondwike.

Head Master, Upper School, Heckmondwike, Yorkshire. Fellow Soc. Chem. Industry. Certificated (First Class) by the Science and Art Department as a Teacher of Chemistry (Theoretical and Practical) and the allied Sciences—Sound, Light, and Heat, Electricity and Magnetism, Physiography, Mechanics; also of Mathematics, Botany, Biology, &c.

George Collar, B.A., B.Sc. Wm. B. Hards, B.A.
James Hall, B.A., B.Sc. *H. R. Hind.* *J. H. Gladstone.*

Wilkinson, David,

Dunedin, Otago, New Zealand.

Lecturer on Metallurgy, &c., Otago University, N.Z. Associate of the Royal College of Science, London, in Physics. Associate Royal School of Mines in Metallurgy. Bessemer Medallist, R.S.M., 1890.

T. E. Thorpe. F. R. Japp. Chapman Jones.
Alfred E. Tutton. William Tate. Edwin J. Ball.

Wyatt, Thomas M.,

20, Queen Square, W.C.

Analytical Chemist. Associate of the Normal School of Science (in Chemistry). Assisted Dr. A. Wright for some months in research work "on Alloys."

T. E. Thorpe. Chapman Jones. F. R. Japp.
Alfred E. Tutton. C. R. Alder Wright.

Wellington, Stephen Newcombe,

Riverdale House, Brundall, Norfolk.

Chemist to British Gas Light Company, Norwich, and Gas Engineer. Chemist to the British Gas Light Company at their Norwich Stations, where they have a well-fitted laboratory; also at their Yarmouth Tar and Ammonia Works. This post has been held by him for three years, during which time he has had constant access to Mr. Sutton's laboratory for experience and practice in analyses connected with gas manufacture. He has also had practical experience in the laboratory of the late B. Nickels, F.I.C., F.C.S., for special analysis of coal-tar products.

Francis Sutton. Wallace C. Nickels. F. A. Manning.
Henry Bassett. *John R. Skelton.*

Will, Dr. W.,

Berlin, N.W., Beethovenstrasse, 1.

Privatdozent a. d. Universität Berlin. Chemische Untersuchungen über Glükoside und Alkaloide, analytisch-chemische Arbeiten veröffentlicht in den Berichten d. deutsch-chem. Gesellschaft. IIter Schriftführer d. deutsch-chem. Gesellschaft.

A. W. v. Hofmann. Ferd. Tiemann. E. Erlenmeyer.
H. Wilson Hake. *A. Dupré.* *John M. Thomson.*

HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY, ST. MARTIN'S LANE.

Issued 18/2/1891.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 92. Session 1890-91.

February 5th, 1891. Dr. W. J. Russell, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. Albert Edward Bell, Sherborne School, Sherborne, Dorset; Rhys Pendrill Charles, Plas Newydd, Neath; Gilbert John Fowler, Dalton Hall, Victoria Park, Manchester; Berington H. Gibbins, Ocala, Florida, U.S.A.; J. A. R. Greaves, Old Rectory, Grappenhall, Cheshire; William Beaumont Hart, Gransmoor Avenue, Fairfield, near Manchester; Rev. Edgar Norman Langham, M.A., St. John's College, Cambridge; James Leicester, 3, Queen's Parade, Brandon Hill, Bristol; William Macdonald, 109, Crofton Road, Peckham, S.E.; Frederick Johnson Merrils, 65, Roe Lane, Pitsmoor, Sheffield; George R. Morrison, Richmond House, Plaistow; Lewis Ough, 15, Upper King Street, Leicester; James Ashburner Storey, Moorside, Lancaster; Albert Searl, The Caxtons, Miskin Road, Dartford.

It was announced that the following changes in the Council list were proposed by the Council:—

As *President*, Professor Crum Brown, *vice* Dr. Russell.

As *Vice-Presidents*, Mr. J. Pattinson and Professor Tilden, *vice* Professors Crum Brown and Mallet.

As *Foreign Secretary*, Professor Meldola, *vice* Professor Japp.

As *Members of Council*, Dr. Atkinson, Mr. Boverton Redwood, Professor Perkin and Dr. J. Voelcker, *vice* Mr. Cross, Professor Dunstan, Professor Meldola and Dr. Plimpton.

The following papers were read:—

5. "The formation of an explosive substance from ether." By Professor P. T. Cleve.

The author, in the course of a letter to the Secretary, describes a

remarkable explosion occasioned by impurities in commercial ether. On distilling about 250 c.c. of the ether, it was noticed that a viscid residue remained; after drying on the water bath, this formed a transparent, amorphous mass, estimated to weigh about 0·75 gram. Professor Cleve states that, having poured a little water on to the substance, he proceeded to stir it gently with a rounded glass rod; this occasioned a most violent explosion. A number of the pieces of glass which were projected about perforated the windows just as if they had been revolver bullets. The explosive substance was probably ethyl peroxide, as it gave the well-known perchromic coloration, besides liberating iodine and discharging oxygen from silver oxide; it was at once destroyed by reducing agents; it exploded with as much violence as if it had been chloride of nitrogen or fulminate.

Discussion.

Professor Dunstan remarked that several cases had been recorded of explosions during the distillation of impure ether, one a few years ago by Schaer in the *Archiv der Pharmacie* for 1877.

6. "Does magnesium form compounds with hydrocarbon radicles?" By Orme Masson, M.A., D.Sc., and U. T. M. Wilsmore, B.Sc., University of Melbourne.

According to Hallwachs and Schafarik (*Annalen*, **109**, 206), magnesium in the form of filings and ethyl iodide commence to interact at ordinary temperatures, and the interaction is complete at 180°; they state that the metal becomes converted into a white mass, the liquid disappearing, much gas being generated. On heating the white mass, a colourless, volatile liquid distilled over, which fumed strongly in the air but did not inflame; this liquid, it was believed, consisted of hydrocarbons mixed with traces of magnesium ethide, but, as the residue decomposed water with explosive violence, it was thought that it contained a considerable amount of magnesium ethide combined with magnesium iodide.

Cahours (*Annales de Chimie et de Physique* [5], **18**, 17) also found that much heat was evolved on adding methyl or ethyl iodide to magnesium filings. Having digested a mixture of the metal and ethyl iodide at 130° till the liquid had disappeared, he heated the resulting white mass in an atmosphere of hydrogen, and obtained a liquid distillate which took fire in the air and acted strongly on water. Carbon and hydrogen were estimated in two fractions of this liquid, but the results were far from agreeing with the theoretical values; the discrepancies were attributed to insufficient purification. No evidence of the presence of magnesium in the product was adduced by Cahours.

Wanklyn heated sodium zinc ethide with mercury and magnesium wire, and obtained a white, spontaneously inflammable, solid product. This contained magnesium and zinc, but only traces of sodium; it was believed to be magnesium zinc ethide.

The authors state that they have in vain endeavoured to prepare magnesium ethide (1) from magnesium and ethyl iodide; (2) from magnesium-copper couples and ethyl iodide; (3) from an alloy of magnesium and sodium and ethyl iodide; (4) from magnesium and zinc ethide; (5) from magnesium and mercury ethide; and (6) from anhydrous magnesium iodide and zinc ethide.

An alloy formed by heating magnesium and sodium together in a hard glass flask in an atmosphere of hydrogen acted very slowly on ethyl iodide at 100°, and no signs of the formation of magnesium ethide were observed. On heating together magnesium and zinc or mercury ethide in sealed tubes, no action occurred till the temperature rose sufficiently high to decompose the ethide; large quantities of gas were then formed, zinc or mercury separating, but no magnesium ethide. Similarly, magnesium iodide and zinc ethide appeared not to interact, the ethide being decomposed simply by the heat.

There appeared to be little or no advantage in using magnesium-copper couples, the action being in all respects similar to that of magnesium alone, although occasionally somewhat quicker. Magnesium iodide and gaseous hydrocarbons were the sole products.

Several experiments on the action of ethyl iodide on magnesium were tried under varied conditions and using the two substances in different proportions; sometimes a crystal of iodine was added as recommended by Frankland for the preparation of zinc chloride. In most cases the materials were heated together in a flask connected to a reflux condenser, from which the air was displaced at the outset by hydrogen or carbon dioxide. The magnesium used was prepared by fusing commercial ribbon in an iron crucible under a flux of ammonium, magnesium and potassium chlorides, and subsequently filing down the lump; it was practically free from impurities except traces of iron. The results obtained were uniformly negative, and although previous observers have stated that interaction occurs at ordinary temperatures, the authors have never perceived the slightest sign of action till after the iodide and metal had been heated together for some time. Thus in an experiment in which 30 grams of specially dried ethyl iodide was added to 5 grams of magnesium, and the temperature of the bath containing the flask was maintained a little below 100°, no action seemed to take place for a time, but after a while gas was given off and a white powder was seen to slowly form on the metal; after 30 hours' continuous heating, ethyl iodide ceased to run back, and the evolution of gas —

which had been continuous—came to an end. On heating the residue to 270°, no distillate except a little unused iodide was obtained; the residue proved on analysis to be simply magnesium iodide. In no case was a trace of distillate obtained showing any tendency to fume in the air. The authors point out that magnesium iodide is very hygroscopic, and is so violently acted on by water that they are inclined to think that Hallwachs and Schafarik may possibly have been led to suppose that magnesium ethide in combination was present when really there was only magnesium iodide. Magnesium iodide forms a crystalline compound with ether which apparently has the composition $MgI_2 \cdot 2Et_2O$.

The authors are hence inclined to conclude that previous experimenters have used magnesium containing some impurity which facilitated its action on the iodide; but they do not see reason for assuming that the result was the production of magnesium ethide. They also suggest that possibly the magnesium previously used may have contained zinc, and that small quantities of zinc ethide mixed with hydrocarbons may have been mistaken for magnesium ethide.

The results, however, raise a question of no slight interest. Of the elements of the second natural group, zinc and mercury very readily form compounds with hydrocarbon radicles; cadmium appears to be capable of forming them though much less readily; and beryllium propide and ethide have been described by Cahours. Calcium, strontium and barium, on the other hand, presumably do not form such compounds. In which sub-group must magnesium be placed according to this test? Again, aluminium, which follows magnesium in series, forms well defined compounds with hydrocarbon radicles, while sodium, which precedes it, forms only an unstable double compound with zinc and ethyl. Which does magnesium resemble, if either? Or has it an intermediate character? It is exceptional for elements on the descending portions of the curve of atomic volumes to unite with hydrocarbon radicles, and a glance at the curve shows that beryllium and magnesium are the only elements undoubtedly occupying such a position that are believed to do so. As to beryllium, it may be pointed out that Cahours (*Compt. rend.*, **76**, 1383) worked with very small quantities and apparently based his conclusions on purely qualitative observations. With regard to magnesium, the authors think that the extremely slight character of the older evidence and the fact that their own experiments have led to directly contrary conclusions to those of Cahours justify them in denying its power to form free compounds of the kind discussed. It is, however, just possible that, as indicated by Wanklyn's qualitative experiment, magnesium may form an unstable double ethide with

zinc, thus resembling sodium, which immediately precedes it in the natural classification.

Discussion.

Dr. Armstrong said that Messrs. Masson and Wilsmore's paper had been despatched from Melbourne on December 29th; meanwhile the question which they had put, and to which they inclined to give a negative reply, had been answered in the affirmative by Löhr in one of the latest numbers of *Liebig's Annalen* (**261**, 72). Löhr, like the authors, had found that methyl and ethyl iodides had no action at ordinary temperatures either on magnesium alone or on magnesium associated with copper or sodium; and that the action was very sluggish at high temperatures. The presence of a little ethylic acetate served, however, to cause an interaction to set in vigorously in the cold, which was completed within 40 to 50 hours at 110°; but the product gave no liquid distillate even at 330°, and Löhr had established the interesting fact that magnesium methide and ethide were solid, non-volatile compounds.

These observations, taken in conjunction with those of the earlier workers in the same field, afforded further evidence that in the formation of organo-metallic compounds, as in so many other cases, it was necessary that some third substance should be present to condition interaction.

Referring to the authors' suggestion, that the magnesium used by previous workers contained zinc, Professor Thorpe said that he had had occasion when at the Owens College to analyse a large number of samples of magnesium from Mr. Sonstadt, who in those days was the sole maker of the metal, and these never contained zinc, so that he could not agree with the authors in their explanation.

7. "Compounds of the oxides of phosphorus with sulphuric anhydride." By R. H. Adie, B.A.

The author has endeavoured to prepare compounds of phosphorus similar to those which the other elements of the group form with sulphuric anhydride.

Employing a preparation obtained from Messrs. Harrington, of Cork, approximately consisting of H_3PO_3, he obtained, by the action of sulphuric anhydride, a product very nearly of the composition corresponding to the formula $H_3PO_4{\cdot}3SO_3 = (SO_3H)_3PO_4$, in the form of a viscid liquid which was decomposed by water, but without violence, yielding sulphuric and orthophosphoric, and but traces of meta- and pyro-phosphoric acids. Sulphuric anhydride and phosphorus were found to interact violently; the author represents the

product by the formula $3P_2O_4{\cdot}2SO_3$. The compound slowly decomposes into phosphoric and sulphurous anhydrides; it is instantly decomposed by water, but the phosphorus containing part dissolves only very slowly.

Discussion.

Professor Ramsay, after referring to the interest attaching to the investigation of compounds such as were described by the author, expressed the opinion that they were legitimately regarded as salts, and that the existence of such salts must serve to break down the distinction which was usually made between metals and non-metals based on the formation of salts.

Professor Thorpe dissented from this view. He also took occasion to correct the statement made by Mr. Tutton and himself, that the oxide P_4O_6 becomes red on exposure to light; this change, they had since discovered, was due to the presence of a small quantity of phosphorus.

8. "Combustion of magnesium in water-vapour." By G. T. Moody, D.Sc.

The author points out that the combustion of magnesium in water-vapour, which is very difficult to conduct in the manner commonly described (*cf.* Kessler, *Ber.*, **2**, 369), may be conveniently demonstrated, as a lecture experiment, by carrying out the operation in a piece of hard glass tube, of about 10 mm. in diameter and 250 mm. in length, bent at an angle of 120° so as to leave one arm nearly twice as long as the other. The shorter arm is inserted through a cork closing the mouth of a "tin-can" or other convenient vessel, in which steam can be generated; and the longer arm, which contains a few strips of magnesium ribbon, is connected by a fairly wide delivery tube with the pneumatic trough, at which the liberated hydrogen may be collected. When the air in the apparatus has been displaced by a slow current of steam, the arm in the tube containing the magnesium is cautiously heated by means of a bunsen burner until the temperature of the tube is considerably higher than that at which water-vapour condenses; the bunsen burner is then replaced by a blowpipe flame, which is moved about in such a way that the whole of the arm becomes very hot, and on allowing the flame to impinge for a few seconds on a portion of the tube against which the magnesium rests, the metal takes fire and burns with great brilliancy.

The success of this experiment is only assured when there is a *very slow* current of steam passing through the apparatus, and when the tube containing the magnesium is carefully heated, as in the manner

above described. Under such circumstances, the metal burns with great regularity, fracture of the tube being usually avoided, and the whole of the hydrogen evolved may be collected.

At the next meeting, on February 19th, there will be a ballot for the candidates whose names and qualifications were set forth in the last number of these Proceedings.

The following papers will be read:—

"The synthesis of dimethyldihydroxyheptamethylene." By Dr. Kipping and Professor Perkin.

"The osmotic pressures of salts in solution." By R. H. Adie, B.A.

CHEMICAL SOCIETY'S JUBILEE.

Fellows are requested to note—

That the afternoon meeting on February 24th will be held in the Theatre of the London University, Burlington Gardens, W., at 3 till 5 o'clock P.M.; the number who have announced their intention of attending being larger than can be accommodated at the Society of Arts.

The presence of ladies is desired.

The President and Council will hold a reception in the evening at 8.30 o'clock, in the Hall of the Goldsmiths' Company, Foster Lane, E.C., the use of which, for the purpose, has been kindly granted to them by the Worshipful Company of Goldsmiths.

On February 25th, the Fellows and their friends will dine at the Whitehall Rooms, Hôtel Métropole, at 6.30 for 7 o'clock. Price of dinner tickets, One Guinea, to be paid in advance. Fellows desiring to be present, who have not yet made application for dinner tickets, are urgently requested at once to give the necessary notice.

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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 93. Session 1890-91.

February 19th, 1891. Dr. W. J. Russell, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. Walter Johnson Cooper, High Street, Mitcheldean, Gloucester; Charles F. Forshaw, LL.D., D.Sc., Bradford, Yorks; John Alfred Foster, Royal Naval College, Greenwich; Claude Hooper Bater, 4, Westbank Terrace, Gibson Street, Hillhead, Glasgow; William L. Hiepe, Ph.D., 21, Acomb Street, Manchester; F. Stanley Kipping, Ph.D., D.Sc., 7, Milborne Grove, South Kensington; Charles Ainsworth Mitchell, 27, Farnley Road, South Norwood; Percy Morrice Randall, 3, Belsize Park Gardens.

Messrs. Holland Crompton, R. H. Davies and Bernard Dyer were appointed by the meeting to audit the Treasurer's accounts.

The following were duly elected Fellows of the Society:—Messrs. John Charles Aydans; Henry Austin Appleton; Charles Norrish Adams, M.A.; John Frederick Bloomer; Clayton Beadle; Robert John Brown; Thomas Byrne; Arthur Cole, B.A.; Arthur Colefax, B.A., Ph.D.; Charles Henry Corbett; Hendrie Thomas Donovan; Robert Bond Greaves; Ernest F. Hooper; Frederick William Harrold; Moses William Jones; Henry Charles Jenkins; Frederick Herbert Moore; Reginald Tom Marshall; Edgar J. Millard; William Morley Martin; Arnold Whitaker Oxford; Michael Samuel Pickering; William Jackson Pope; Tom Kirke Rose; R. Stockdale; Matthew Carrington Sykes; Herbert D. Shaw; R. Greig Smith; Kenelm Edward Symes; Howard C. Sucré; A. H. Tapp; Frederick William De Velling, B.A.; David Wilkinson; Thomas M. Wyatt; Stephen Newcombe Wellington; Dr. W. Will.

The following papers were read:—

9. "The action of reducing agents on $\alpha\alpha'$-diacetylpentane. Synthesis of dimethyldihydroxyheptamethylene." By F. Stanley Kipping, Ph.D., D.Sc., and W. H. Perkin, Jun., Ph.D., F.R.S.

On reducing $\alpha\alpha'$-diacetylpentane, $COMe{\cdot}[CH_2]_5{\cdot}COMe$ (Trans., **56**, 330), dissolved in moist ether, with sodium, it is converted into a colourless liquid of the composition $C_9H_{18}O_2$. The method of preparation, properties and some derivatives of this reduction product are described in the paper, and also various experiments made with the object of determining its constitution.

The authors' investigations have shown that the reduction product must be regarded as a dimethyldihydroxyheptamethylene of the constitution $CH_2<\begin{matrix}CH_2{\cdot}CH_2{\cdot}C(OH){\cdot}CH_3\\ CH_2{\cdot}CH_2{\cdot}C(OH){\cdot}CH_3\end{matrix}$.

This conclusion is based on the following considerations:—The reduction product is formed by the addition of two atoms of hydrogen to diacetylpentane, and may, therefore, theoretically have the constitution represented by one of the following formulæ:—

I. $CH_2<\begin{matrix}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3\\ CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_3\end{matrix}$. II. $CH_2<\begin{matrix}CH_2{\cdot}CH_2{\cdot}C(OH){\cdot}CH_3\\ CH_2{\cdot}CH_2{\cdot}C(OH){\cdot}CH_3\end{matrix}$.

As in the one case the compound would be an open-chain ketone alcohol (Formula I), and in the other a dihydroxy-derivative of a closed carbon chain (Formula II), it is comparatively easy to ascertain which of the two formulæ represents the constitution of the compound. (1.) The reduction product does not combine with hydroxylamine, or with phenylhydrazine. (2.) It yields a diacetyl derivative of the composition $C_{13}H_{22}O_4$ with acetic anhydride. (3.) Phosphorus pentabromide converts it into a dibromide of the composition $C_9H_{16}Br_2$. (4.) It is not acted on by such reducing agents as zinc and chlorhydric acid, sodium amalgam, or sodium and alcohol. (5.) On reduction with hydrogen iodide, it is converted into a hydrocarbon of the composition C_9H_{18}.

These facts, the authors think, are sufficient to warrant the conclusion that the reduction product is a dimethyldihydroxyheptamethylene of the constitution given above.

Dimethyldihydroxyheptamethylene, $C_9H_{18}O_2$, is a thick, colourless liquid, boiling at 201° (180 mm.); it is only sparingly soluble in cold water, but miscible with alcohol, ether &c. in all proportions. The *sodium* derivative, $C_9H_{17}O_2Na + H_2O$, is a colourless, semi-crystalline, very deliquescent compound.

Dimethyldibromoheptamethylene, $C_9H_{16}Br_2$, prepared by treating the dihydroxy-compound with phosphorus pentabromide in chloroform solution, is a thick, colourless oil.

Dimethylhydroxyiodoheptamethylene, $C_{19}H_{17}OI$, is formed when the glycol is heated with hydrogen iodide; it is a colourless liquid, with a pleasant, sweetish smell.

Dimethylheptamethylene diacetate, $C_9H_{16}(OAc)_2$, is obtained when the dihydroxy-compound is boiled with acetic anhydride; it boils at 199—202° (65 mm.) and is readily hydrolysed by dilute soda.

Dimethylheptamethylene, C_9H_{18}, is obtained in the form of a colourless, mobile oil when dimethyldihydroxyheptamethylene is heated with hydriodic acid and amorphous phosphorus; it boils at 153—154° and has an odour very like that of light petroleum.

Discussion.

Dr. Armstrong and Dr. Collie both drew attention to the possible formation of a hexamethylene compound by reduction of the diketone diacetylpentane, and asked what evidence other than synthetical established the constitution of the reduction product.

Dr. Kipping, while admitting that at present there was no such evidence, contended that the formation of a hexamethylene compound was altogether improbable.

10. "The osmotic pressures of salts in solution." By R. H. Adie, M.A.

This paper contains the experimental results of an investigation of the osmotic pressures of salts in solution by direct observation, by the method of Pfeffer. The results are arranged under five headings.

1. *Boyle's Law applied to solutions.*—The observations are plotted out with osmotic pressures for ordinates and concentrations (in terms of gram molecules per litre) for abscissæ. The salts observed were potassium and sodium nitrates, potassium iodide, potassium sulphate, potash alum, potassium ferrocyanide and cobalticyanide and a few others. The results obtained show that the osmotic pressures do not vary directly as the concentrations, but take a definite curved form, approaching Ostwald's line of no dissociation at two points, and receding from it elsewhere. Potash alum gives the nearest approach to a straight line of the salts examined.

2. *Charles's Law applied to solutions.*—Only one experiment yielded any result, and that was confirmatory of the correctness of applying Charles's Law to solutions.

3. *Influence of bases on osmotic pressures.*—No definite influence can be attributed to the base, except that the salts of some bases, *e.g.*, soda, appear to be more readily dissociated by water than those of others, *e.g.*, potash.

4. *Influence of acids on osmotic pressures.*—In the case of inorganic acids, no very definite influence can be detected; though the equiva-

lents of the salts of monobasic acids give in general higher osmotic pressures than those of the salts of dibasic acids. In the case of organic acids, an increase in the molecular weight of homologous acids increases the osmotic pressure, and a ring nucleus gives a higher osmotic pressure than an open chain.

5. *Avogadro's Law applied to salts in solution.*—The author examines and compares the differences between the observed results and those calculated on the assumption that Avogadro's Law applies to salts in solution, and suggests that they may be due, as in Crookes' hypothesis, to the existence of simple and complex molecules in solution, as well as to the formation of water compounds in the solution. This hypothesis does not appear to require so large a modification of ordinary chemical ideas as that of Ostwald and Arrhenius.

11. "A direct comparison of the physical constants involved in the determination of molecular weights by Raoult's method." By R. H. Adie, M.A.

In this paper, the author tries to connect the constants of Raoult's method of determining molecular weights of a substance in solution with those ascertained by direct observation of the osmotic pressure of the same solution. Also, by the same method of Raoult, to connect the osmotic pressure with the gaseous pressure of any substance in solution. The substances chosen are potassium iodide and ammonia. The solutions of potassium iodide and ammonia are compared by means of the lowering of the freezing point, and then the osmotic pressures of the same solutions of potassium iodide are given. The author shows that the constants obtained by the two methods do not agree, and suggests an hypothesis to explain the same, which is given above.

Discussion.

Mr. Pickering said that the numerous results brought forward by Mr. Adie could not fail to be of value. They seemed to afford fresh proof of the irregularities almost invariably shown by the properties of solutions, where, according to the physical theory, there should be nothing but regularity and uniformity. It was to be regretted that the determinations had not been pushed further into the region of dilute solutions, for it was here that some of the most surprising irregularities existed, and it was here that the existence of such must tell most strongly against any purely physical theory. Mr. Adie had touched on one of the most fundamental objections to the present physical theory of solution—the existence of osmotic pressure—for this is due to the impermeability of a membrane to the dissolved substance; and how can it be contended that if the molecules of the

latter were single, and still more if they were dissociated into ions, they cannot get through holes which the water molecules have no difficulty in threading?

12. "Derivatives of piperonyl." By Frederick M. Perkin.

The author describes the results of experiments made with the object of determining the constitution of the compound $C_{10}H_9NO_3$ obtained by his brother from berberine (Trans., 1890, 992), a knowledge of which was essential to the determination of the nature of this alkaloïd; two formulæ would account for the properties of the substance, viz.:—

$$CH_2<\begin{matrix}O\\O\end{matrix}>C_6H_2<\begin{matrix}NH\cdot CO\\ |\\ CH_2\cdot CH_2\end{matrix} \qquad CH_2<\begin{matrix}O\\O\end{matrix}>C_6H_2<\begin{matrix}CO\cdot NH\\ |\\ CH_2\cdot CH_2\end{matrix}.$$

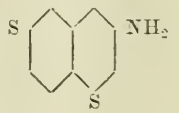
The second of these is found to be applicable to the substance in question. In the present paper, the author describes the preparation of the compound represented by the first formula from piperonal. On heating a mixture of nitropiperonal, acetic anhydride and sodium acetate, an acid was obtained identical with that formed on nitrating the piperonylacrylic acid of Lorenz. On reduction with ferrous sulphate, this nitro-acid is converted into the corresponding amido-acid, but when zinc or tin and muriatic acid is used, the anhydro-derivative of the amido-acid is obtained.

The action of bromine on piperonylacrylic acid is described, and also the formation of a benzoin-like compound from piperonal and potassium cyanide.

13. "Studies on the constitution of tri-derivatives of naphthalene, No. 9. Andresen's β-naphthylaminedisulphonic acid." By Henry E. Armstrong and W. P. Wynne.

According to Schultz (*Ber.*, **23**, 77), naphthalene-1 : 3′-disulphonic acid on nitration yields a mixture of several nitronaphthalenedisulphonic acids. The chief product on reduction gives the so-called α-naphthylamine-ϵ-disulphonic acid [$NH_2 : SO_3H : SO_3H = 1' : 1 : 3'$; *v.* Armstrong and Wynne, these Proc., 1890, 15] of the Germ. Pat. 45776. Of the other acids, the production of which has been also noted by Bernthsen (*Ber.*, **23**, 3088, footnote), one yields on reduction, according to Schultz, a β-naphthylaminedisulphonic acid. As this was the first instance in which the formation of a *beta*-nitro-acid by the nitration of a naphthalenesulphonic acid had been observed, the attention of the authors was directed to the determination of its constitution, and through the liberality of the Actiengesellschaft für Anilinfabrikation a considerable supply of the material remaining after the separation of the greater part of the ϵ-acid was placed at

their disposal for examination. After separation from the associated acids, and comparison with a specimen of the pure Andresen acid received from Dr. Schultz, the amido-acid was analysed by the hydrazine and Sandmeyer methods already described. When reduced by the hydrazine method, it gave naphthalene-1 : 3′-disulphonic acid, which was characterised by means of its chloride, $C_{10}H_6(SO_2Cl)_2$, melting at 127°, and the derived 1 : 3′-dichloronaphthalene melting at 48°. On treatment by the Sandmeyer process, it was converted into a chloronaphthalenedisulphonic acid, the chloride of which, $C_{10}H_5Cl(SO_2Cl)_2$, crystallised from benzene in radiate groups of flat needles melting at 174°, and on distillation with PCl_5 yielded 1 : 3 : 3′-trichloronaphthalene melting at 80·5°. This acid, consequently, was identical with that obtained by the authors by sulphonating 2 : 2′-β-chloronaphthalenesulphonic with 20 per cent. anhydrosulphuric acid (these Proc., 1890, 133). As a further proof of the identity of the two compounds, the chloronaphthalenedisulphonic chloride derived from the Andresen acid was hydrolysed by heating with dilute sulphuric acid at 250—270° for several hours, with the result that β-chloronaphthalene melting at 59·5° was obtained. Combining these results, it follows that the Andresen acid *is* a β-naphthylaminedisulphonic acid of the constitution—



The salts of this 2 : 4 : 2′-β-naphthylaminedisulphonic acid, and the mode of separation from the other naphthylaminesulphonic acids contained in the mixture, will be described when the examination of the nitration product of naphthalene-1 : 3′-disulphonic acid has been completed.

At the next meeting, on March 5th, the following papers will be read:—

"Chloro- and bromo-derivatives of naphthol and naphthylamine." By Dr. Armstrong and E. C. Rossiter.

"The crystalline form of the calcium salt of optically active glyceric acid." By A. E. Tutton.

"Fermentations induced by the *Pneumococcus* of Friedlaender." By Prof. P. F. Frankland, A. Stanley and W. Frew.

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PROCEEDINGS

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No. 94. Session 1890-91.

March 5th, 1891. Dr. W. J. Russell, F.R.S., President, in the Chair.

Mr. A. W. Oxford was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. William Bate, National Explosives Company, Hayle, Cornwall; Alexander Lauder, University College, Bangor, North Wales; Cecil George Freer Thonger, Colonial College, Hollesley Bay, Suffolk.

The following papers were read:—

14. "Crystalline form of the calcium salt of optically active glyceric acid." By Alfred E. Tutton, Royal College of Science, London.

This paper presents the results of a complete crystallographical investigation of the calcium salt, $Ca(C_3H_5O_4)_2,2H_2O$, of the optically active (dextrorotatory) form of glyceric acid described (Trans., 1891, p. 96) by Frankland and Frew. The crystals belong to the monoclinic system, and are hemihedral, the forms $\{111\}$ and $\{011\}$ being only developed at the right-hand extremity of the symmetry axis, and the forms $\{\bar{1}\bar{1}1\}$ and $\{\bar{2}\bar{1}1\}$ at the left extremity. The hemihedrism is also manifested by a difference in the prism faces of the form $\{110\}$, those upon the right side of the symmetry plane being much more brilliant than those upon the left side. The ratio of the axes is $a : b : c = 1{\cdot}4469 : 1 : 0{\cdot}6694$. A complete table of angles is given, the result of the measurement of a dozen crystals. The optic axial plane is perpendicular to the symmetry plane, and the first median line is nearly perpendicular to the basal plane. The true angle of the optic axes is $2Va_{Li} = 34^\circ\ 56'$, $2Va_{Na} = 35^\circ\ 28'$,

$2Va_{Te} = 36° 16'$. The mean refractive index β is 1·4496, 1·4521 and 1·4545 for lithium, sodium and thallium light respectively. The sign of double refraction is positive. The calcium salt of this dextrorotatory glyceric acid must therefore be added to the list of optically active substances whose crystals are also hemihedral, a list which includes all the hitherto well investigated cases.

15. "Fermentations induced by the *Pneumococcus* of Friedländer." By Percy F. Frankland, Ph.D., B.Sc. (Lond.), Arthur Stanley and Wm. Frew.

That this well known micro-organism is capable of inducing fermentative changes in suitable solutions of glucose and cane-sugar was first pointed out by Brieger (*Zeit. f. physiol. Chem.*, 8, 306—331, and 9, 1—7). The authors have confirmed these observations of Brieger's, and have further found that the organism ferments maltose, milk-sugar, raffinose, dextrin and mannitol, but that, like the *Bacillus ethaceticus*, it does not attack dulcitol. They have made a special study of the fermentations of glucose and mannitol, determining quantitatively the proportions in which the several products are formed. These products are in each case ethyl alcohol, acetic acid, generally accompanied by a little formic acid and a trace of succinic acid, carbon dioxide and hydrogen. Both the glucose and mannitol were in all cases only partially fermented, and the decomposition of the glucose was especially incomplete, glucose being apparently less readily attacked by the organism than mannitol and cane-sugar. The fermentation was not rendered more complete by furnishing the organism with a more abundant supply of nitrogenous food.

In the first instance, fermentations were conducted on 60 grams of glucose and mannitol respectively, with the following results:—

	I. Glucose.	II. Mannitol.	III. Mannitol.
Ethyl alcohol	0·5897 gram	4·11 grams	5·06 grams.
Volatile acids calculated as acetic acid	1·6578 ,,	2·9921 ,,	3·1617 ,,

The products of the mannitol fermentations are not only qualitatively similar to those obtained in the fermentation of the same substance by the *Bacillus ethaceticus*, but the relative proportions in which they are formed are almost identical, the ratio corresponding closely to the molecular proportions $2C_2H_5{\cdot}OH : CH_3{\cdot}COOH$.

In the subsequent experiments, in which the volume and composi- of the evolved gases were determined, only 12 grams of mannitol were employed; in this case also very similar ratios were obtained,

although a period of two years had elapsed since the above fermentations had been carried on.

The following results of analysis show the composition of the gas evolved in a fermentation with 12 grams mannitol, after the air in the apparatus had been displaced :—

	16th day.	23rd day.	34th day.	41st day.	Average.
CO_2	51·77	61·29	66·18	65·47	61·18
O_2	0·09	0·15	0·22	0·09	0·14
H_2	47·97	38·26	33·47	34·19	38·47
N_2	0·17	0·30	1·13	0·25	0·21
	100·00	100·00	100·00	100·00	100·00

The lower proportion of carbon dioxide in the earlier part of the fermentation is doubtless due to the liquid saturating itself with the gas, and the excess at the end to the slow decomposition of the calcium bicarbonate formed in the first instance. The average composition of the gas may be taken to be 6 volumes or molecules of carbon dioxide to 4 volumes or molecules of hydrogen. Taking into account the actual volume of gas given off, the several products are in very close accord with the molecular proportions: $9C_2H_6O$. $4C_2H_4O_2$: $12CO_2$: $8H_2$, derived from 6 mol. props. of mannitol, 2 mol. props. of carbon dioxide being formed by the action of the acetic acid on the added calcium carbonate.

By plotting out the volumes of evolved gas on a diagram, in which the ordinates represent the volumes in cubic centimetres, and the abscissæ the time of fermentation in days from the date of inoculation, the authors obtain a curve for which the equation is

$$v = \frac{6{\cdot}73t^2}{1 - 0{\cdot}006t + 0{\cdot}00574t^2}.$$

16. "The volumetric estimation of tellurium. Part II." By B. Brauner, Ph.D.

The author finds that although a solution of iodine in potassium iodide acts on alkaline tellurates in accordance with the equation $Na_2TeO_3 + I_2 + 2NaOH = Na_2TeO_4 + 2NaI + H_2O$, the action is very slow and incomplete at the ordinary temperature, so that heat must be applied for its completion. On acidification the excess of iodine is set free, but it has hitherto been found impossible to exactly determine the end of reaction by titration with thiosulphate.

The titration of solutions of tellurium dioxide in chlorhydric acid with permanganate is found to be impracticable, as varying quantities of chlorine are evolved during the process.

When a solution of tellurium dioxide in sulphuric acid is titrated with permanganate, the following interchange occurs:—$2KMnO_4 + 4H_2SO_4 + 4TeO_2 = K_2SO_4 + Mn_2(SO_4)_3 + 4H_2O + 4TeO_3$. In order to destroy the manganic salt which is formed, either decinormal ferrous sulphate or oxalic acid is added until decolorisation takes place, after which permanganate is added in slight excess. After subtracting the volume of permanganate corresponding to the ferrous salt or to oxalic acid from the total of permanganate added, the quantity of tellurium dioxide is calculated from the volume of permanganate necessary for its oxidation, as if the following action had taken place: $2KMnO_4 + 3H_2SO_4 + 5TeO_2 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5TeO_3$. Owing to the evolution of some oxygen, the quantity of tellurium dioxide found is greater by 1 per cent. than that calculated from the equation.

In alkaline solution the change which takes place is that indicated by the equation $2KMnO_4 + 3TeO_2 = K_2O + 2MnO_2 + 3TeO_3$. After addition of an excess of sulphuric acid oxalic acid is used for retitration in the manner previously stated, but the results are 0·35 per cent. too high. The results obtained by both methods are accurate when the corrections mentioned are applied.

17. "Chloro- and bromo-derivatives of naphthol and naphthylamine." By Henry E. Armstrong and E. C. Rossiter.

This communication is a continuation of one published in these Proceedings in 1889.

1 : 4-*Dichloro-β-naphthol.*—A better yield of this compound than is obtained by Zincke's method appears to result from the gradual interaction of chloro-β-naphthol and sulphuryl chloride at ordinary temperatures, about 30 per cent. of the chloro- being converted into the dichloro-compound. The mixture obtained on steam-distilling the crude product is sulphonated, and the mixture of salts resulting from the direct neutralisation of the acid solution with potassium carbonate is extracted with boiling alcohol, which dissolves the dichloro- but not the monochloro-sulphonate. The dichloronaphthol is recovered by heating the sulphonate with dilute sulphuric acid at 210°.

1 : 4 : 4′-*Trichloro-β-naphthol.*—The oily by-product obtained in preparing a large quantity of trichloro-β-ketonaphthalene, when allowed to stand during many months, was found to slowly give off hydrogen chloride and to become partially solid; the solid was freed from oil by washing with acetic acid and was recrystallised from this solvent. The substance thus obtained proves to be a trichloro-β-naphthol, and as it yields 1 : 2 : 3-chlorophthalic acid on oxidation,

and is reduced by sodium amalgam to 1 : 4-dichloro-β-naphthol, it is most probably the 1 : 4 : 4′-modification. It crystallises in short, soft needles melting at 157—158°; its acetyl derivative melts at 129°.

Chloro-β-naphtholsulphonic acid.—1-Chloro-, 1 : 3- and 1 : 4-dichloro-, and 1 : 3 : 4′- and 1 : 4 : 4′4trichloro-β-naphthol are all sulphonated with the greatest ease, each yielding a derivative of 1 : 3′- (Schaefer's) β-naphtholsulphonic acid, proof that this is the case being afforded by the formation of this acid from each of the chloro-acids on reduction. This result is noteworthy inasmuch as 3′ : 1-dibromo- and bromochloro-β-naphthol—in which the position occupied by the sulpho-group in Schaefer's acid is occupied by bromine—are distinctly less readily sulphonated than any of the chloronaphthols referred to; and it is a matter of interest also that neither is a derivative of the Weinberg β-acid, isomeric with Schaefer's, formed from them; hence it would seem that a β-sulphonic acid only results when the β- 3′-position is free, viz., that which is symmetrically situated relatively to the β-OH group.

1 : 3′-*Dibromo-* and *bromochloro-β-naphthol.*—In the previous communication it was stated, that on brominating either bromo- or chloro-β-naphthol, the bromine is introduced into the second nucleus. To determine the position taken up by the bromine, the bromochloronaphthol was distilled with PCl_5; 1 : 2 : 3′-trichloronaphthalene was one of the products obtained, and it would seem therefore that it occupies the position 3′-. As both dibromo- and bromochloronaphthol afford 1 : 3 : 4-bromophthalic acid on oxidation, this conclusion may be regarded as established. Independent confirmation of this result is afforded by the observation that chloro-β-acenaphthalide is converted by bromine almost quantitatively into a bromochloroacenaphthalide (m. p. 216°), which affords a bromochloronaphthylamine (m. p. 119°) and a bromochloronaphthalene (m. p. 60°) in which the bromine atom occupies the β- 3′-position; also by Claus's recent statement that when brominated bromo-β-acenaphthalide in like manner yields 1 : 3′-dibromo-β-naphthylamine (*J. pr. Chem.*).

The conclusion thus arrived at, however, is in opposition to that to be deduced from Smith's and Meldola's statement, that tetrabromo-β-naphthol, when oxidised, yields the bromophthalic acid whose anhydride melts at 134°, *i.e.*, the 1 : 2 : 3-acid. The authors have, therefore, studied the action of bromine in excess on β-naphthol. They find that, contrary to Smith's statement, the preparation of tetrabromonaphthol is attended with very considerable difficulty, the product chiefly consisting of tribromonaphthol; the separation of this latter by crystallisation is difficult, but is easily accomplished by acetylating the crude product and recrystallising the acetate from benzene and from acetic acid. The acetate crystallises in long, fine

needles melting at 184°, and is very easily hydrolysed. Tribromo-naphthol melts at 155—156°; on oxidation with alkaline permanganate it yields 1 : 3 : 4-bromophthalic acid. The authors are still engaged in investigating this compound and the other products of the action of bromine in excess on β-naphthol.

Action of nitric acid and of oxidising agents on chloro- and bromo-naphthols.—Nearly all the chloro- and bromo-derivatives of β-naphthol yield characteristic quinone derivatives when submitted to the action of nitric acid; in most cases the formation of these is preceded by that of an unstable intermediate compound, the determination of whose composition presents great difficulties. The final product of the action of nitric acid is a phthalic acid. Alkaline permanganate is not always a suitable agent to employ if the object be to completely oxidise the naphthol: thus the main product of its action on dibromo-β-naphthol, for example, is the acid

$$C_6H_3Br<\begin{matrix}CH\\CO\end{matrix}>\!\!\!=\!\!\!=O^{COOH},$$

which, on distillation, yields bromophthalide.

ANNIVERSARY MEETING.

Wednesday, March 25th, at 8 P.M.

At the next meeting, on March 19th, the following papers will be read:—

"The molecular refraction and dispersion of various substances." By Dr. Gladstone, F.R.S.

"Contributions to our knowledge of the aconite alkaloids. Part I. On the crystalline alkaloid of *Aconitum napellus*." By Professor Dunstan and Dr. W. H. Ince.

"The crystallographic characters of aconitine from *Aconitum napellus*." By Mr. A. E. Tutton.

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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 95. Session 1890-91.

March 19th, 1891. Dr. W. J. Russell, F.R.S., President, in the Chair.

Messrs. William Ramsay, Spencer Umfreville Pickering and Edgar J. Millard were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Edward Arthur Barnes, 57, Delafield Road, Charlton, S.E.; Frederick Arthur Evans, Cape Colony, South Africa; Joseph Fitze, 1, New China Bazaar Street, Calcutta; Walter Herbert Joseland, 9, Campbell Grove, Oxford Road, Manchester; John Wild, 28, Hyde Road, Woodley, Stockport.

The following papers were read:—

18. "Molecular refraction and dispersion of various substances." By J. H. Gladstone, Ph.D., F.R.S.

This paper contains a record of a considerable number of hitherto published observations of refractive indices that had accumulated in the author's note book, together with the optical constants calculated from them, and remarks on their bearing on chemical or physical theory.

Observations are quoted on carbon bisulphide and benzene at various temperatures which confirm the old conclusion that the specific refractive energy of a liquid is a constant not affected by temperature.

In a second series of tables the data are recorded relating to a number of carbon compounds mostly prepared by Dr. Perkin; the molecular refraction and dispersion calculated from experiment are

compared with those reckoned from the values already assigned to the constituent elements. In the majority of cases the experimental and theoretical numbers are in fairly close accordance; in some cases, however, there is a discrepancy larger than is likely to be due to experimental error or impurity of substance. This, of course, points to some difference of constitution. Amongst the comments made upon these results the following may be noted:—The molecular dispersion of amylene shows the amount of increase for double-linked carbons which characterises the allyl compounds previously examined, and the allyl and diallylacetic acids in the table. The three modifications of xylene, while differing considerably in their actual indices, have almost identically the same molecular refraction and dispersion.

Safrol agrees in optical properties with what may be termed the normal value reckoning for four double linked carbons; but anethoil, cinnamene and butenylbenzene, though they have only the same number of double linkings, give a refraction, and especially a dispersion, far above what theory requires; thus indicating the presence of carbon in that still more refractive and dispersive condition to which the author drew attention in 1881.

Some of the results, *e.g.*, those relating to the isomeric maleic and fumaric ethers, afford fresh confirmation of the analogy between the molecular refraction and dispersion and the molecular magnetic rotation of the same substance as observed by Perkin.

The nitrogen compounds give results quite confirmatory of the two values previously assigned to that element in combination. The same remark applies to the isomeric ethylic thiocyanate and mustard oil.

The observation of stannic ethide gives a refraction equivalent for tin, 18·1, in fair accordance with that determined from its chloride; but the value of zinc in zincic ethide, 15·9, differs totally from that determined from its dissolved salts.

Observations are also quoted of the halogen compounds of silicon and titanium which tend to confirm the former refraction equivalents, and indicate that the atomic dispersion of silicon is very small, about 0·32; and that of titanium very large indeed, about 8·7.

19. "Contributions to our knowledge of the aconite alkaloids. Part I. On the crystalline alkaloid of *Aconitum napellus*." By Wyndham R. Dunstan and W. H. Ince. Ph.D. (from the Research Laboratory of the Pharmaceutical Society).

The authors have investigated the properties of a crystalline alkaloid obtained from the root of *Aconitum napellus* by extraction with amyl alcohol, as suggested by the late Mr. John Williams. For a supply of the material they are indebted to the kindness of Messrs. Howard and Sons, of Stratford.

The yellowish, indistinct crystals melted at 188·4° (corr.), and by crystallisation from alcoholic solution were proved to be associated with a small quantity of a gummy, amorphous base. On combustion, the original substance gave numbers agreeing fairly well with the formula $C_{33}H_{43}NO_{12}$, which is that proposed for aconitine by Wright and Luff (Trans., 1879). The alkaloid was purified by repeated crystallisation from a mixture of alcohol and ether, or more readily by conversion into its bromhydride and regeneration of the alkaloid from the salt, or by regeneration from its crystalline aurichloride. It crystallises in tabular prisms belonging to the rhombic system; the crystallography of the substance forms the subject of a separate communication from Mr. Tutton. The crystals are very slightly soluble in water and light petroleum, more soluble in ether and alcohol, most soluble in benzene and chloroform. They melt at 188·5° (corr.). Contrary to the statements of previous observers, who found aconitine to be lævo-rotatory, the authors found an alcoholic solution to be *dextro-rotatory*, $[\alpha]_D$ +10·78°; the aqueous solution of the bromhydride is, however, lævo-rotatory, $[\alpha]_D$ −30·47°. On analysis, the alkaloid afforded results which agreed best with the formula $C_{33}H_{45}NO_{12}$.

Two crystalline *aurichlorides* were obtained. One melting at 135·5° (corr.) ($C_{33}H_{45}NO_{12}HAuCl_4$); the other, a basic aurichloride ($C_{33}H_{45}NO_{12}AuCl_3$) melting at 129° (corr.). These compounds are obtained without difficulty, and afford trustworthy means of identifying aconitine. The alkaloid may be readily recovered from them in a pure state.

Aconitine is not appreciably affected by heating at a temperature below its melting point, but at this temperature it is gradually converted into the uncrystallisable base aconine. Prolonged boiling in aqueous solution induces a similar change, but not to the same extent unless an alkali is present. Boiling with water acidulated with chlorhydric acid also produces decomposition of the alkaloid.

Dehydraconitine or *apo-aconitine* is a base differing from aconitine by the absence of a molecular proportion of water which was first obtained by Wright and Luff by acting on aconitine with acids. Its existence has, however, been questioned by later workers. The authors find that such a substance may be readily procured by heating aconitine with saturated aqueous tartaric acid in closed tubes, as recommended by Wright and Luff. The crystals of this substance melt at 186·5° (corr.). It forms crystalline salts, and in other respects closely resembles the parent alkaloid. The results of analyses agree well with the formula $C_{33}H_{43}NO_{11}$. Three *aurichlorides* were obtained: one ($C_{33}H_{43}NO_{11}HAuCl_4$) melts at 141° (corr.); this salt, when crystallised from aqueous alcohol, affords a hydrate

($C_{33}H_{43}NO_{11}HAuCl_4,H_2O$), m. p. 129° (corr.), isomeric with aconitine aurichloride, into which indeed it very readily changes. The third aurichloride is a direct compound of the alkaloid with auric chloride ($C_{33}H_{43}NO_{11}AuCl_3$); it melts at 147·5° (corr.).

An *amorphous base* was obtained from aconitine, together with benzoic acid, by prolonged heating with water in a closed tube. It appears to be identical with the *aconine* of Wright and Luff. The same substance is formed together with a resinous substance when aconitine is heated with an alkali. Neither aconine nor its salts could be crystallised. The amorphous base after purification and its amorphous aurichloride afforded analytical data agreeing with the formulæ $C_{26}H_{41}NO_{11}$ and $C_{26}H_{41}NO_{11},HAuCl_4$ respectively.

A further study is being made of aconine, and of the question as to the existence of other alkaloids in this plant.

Discussion.

Dr. Alder Wright expressed his gratification that the authors so substantially corroborated the results brought before the Society by himself some thirteen years ago. The difference in the results obtained by various chemists he thought was largely attributable to defective methods of isolation of the active principle, whereby the true aconitine became more or less hydrolysed, or otherwise acted on, so as to be transformed into non-crystalline, and comparatively inert, substances; also to the imperfection of the methods adopted for separating the true active crystallisable alkaloid from the non-crystalline and far less active alkaloids naturally accompanying it. It was greatly to be regretted that preparations were largely sold under the name of aconitine of which only a very small fraction actually was aconitine, the greater part consisting of relatively inert, other alkaloids. It was as though a substance should be sold as morphine which almost entirely consisted of narcotine and the other less active opium bases, so that its physiological potency was only a small fraction of that of genuine morphine.

Dr. Thudichum forcibly described the uncertainty and danger attending the use of the drug "aconitine" in medical practice, owing to absence of uniformity in the products of English, French and German manufacture. A final determination of the properties and mode of preparing the active principles of the various kinds of aconite would, he said, be a work of great value.

Professor Dunstan, in reply, said it was well known that the commercial aconitines varied much in toxic power, all of them being more or less impure, chiefly from the presence of amorphous alkaloid, which appeared to be non-toxic. Dr. Waller, of St. Mary's Hospital,

had undertaken to investigate the physiological action of the pure alkaloid obtained in the course of this research. It was intended to fully examine the alkaloids contained in *A. ferox* and *A. saponicum*.

20. "The crystallographical characters of aconitine from *Aconitum napellus*." By A. E. Tutton, Royal College of Science, London.

The author has made a complete crystallographical examination of some fine specimens of aconitine crystals, obtained during the course of the work described in the preceding communication. Aconitine crystallises in the rhombic system. Habit: prismatic, with inclination to tabular, owing to the large development of the brachypinacoid. Ratio of axes: $a : b : c = 0{\cdot}5456 : 1 : 0{\cdot}3885$. Forms observed: $a\{100\}, b\{010\}$, $p\{110\}$, $p'\{120\}$, $m\{101\}$, $q\{021\}$, and $o\{121\}$. A complete table of angles is given in the memoir. There is a good cleavage parallel to $a\{100\}$. Optic axial plane is $b\{010\}$. Aconitine is a highly dispersive substance. The apparent acute angle of the optic axes in air 2E for lithium light is 47° 0′, for sodium light 56° 10′ and for thallium light 65° 5′. Hence there is a dispersion of 18° 5′. The double refraction is positive.

21. "The asymmetry of nitrogen in substituted ammonium compounds." By S. B. Schryver, B.Sc.

Although isomeric compounds in which isomerism is due to the different geometrical arrangement of radicles round the carbon atom have for several years been known, stereo-isomers—to use V. Meyer's term—in which the radicles have different arrangements round a nitrogen atom have not up to the present been conclusively proved to exist. Hantzsch and Werner (*Ber.*, **23**, *et seq.*) have sought to explain the existence of the different hydroxamic acids of Lossen and the mono- and di-benzoxime compounds of V. Meyer and Auwers (*Ber.*, **21**, 784) by the hypothesis that they are stereo-isomers of nitrogen: they suppose that this element is capable of forming compounds the general types of which may be represented by the constitutional formulæ—

$$\begin{matrix} X{-}N \\ \| \\ N{-}Y \end{matrix} \quad \text{and} \quad \begin{matrix} X{-}N \\ \| \\ Y{-}N \end{matrix}, \quad \text{and} \quad \begin{matrix} X{-}N{-}Y \\ | \\ U{-}N{-}Z \end{matrix} \quad \text{and} \quad \begin{matrix} X{-}N{-}Y \\ | \\ Z{-}N{-}U \end{matrix}.$$

This explanation of the isomerism is not accepted by Meyer (*Ber.*, **23**, 603). Moreover, the evidence of the existence of such stereo-isomers in the case of compounds other than the hydroximes and hydroxamic acids is, up to the present, very slight and of a very doubtful nature.

If, however, the compounds of trivalent nitrogen *are* capable of forming such stereo-isomers, we should expect that in compounds

of pentavalent nitrogen, where the opportunity for difference in the relative arrangements of the radicles in the molecule is greater, stereo-isomers should also, *a fortiori*, exist. To produce these has been the primary object of the author's work.

The class of compounds chosen for study was the substituted ammoniums. The tertiary amines easily combine with alkyl iodides without evolution of heat (under suitable conditions), and it is, therefore, possible to obtain well-crystallised compounds, viz., the platinichlorides, *under such conditions that isomeric changes are not likely to take place.*

The author, in conjunction with N. Collie, examined the platinichlorides obtained from the different mixed methyl and ethyl ammonium bases of the formulæ Me_3EtNOH, Me_2Et_2NOH, $MeEt_3NOH$; these were prepared both from triethylamine and also trimethylamine as a starting point. But it did not seem to make any difference in the crystalline form of the platinochlorides, whether the base was prepared from triethylamine or trimethylamine, or whether the solutions were evaporated by the aid of heat or *in vacuo*.

The author has, however, since prepared quaternary ammonium compounds, containing three different radicles—

I. By adding methyl iodide to diethylisoamylamine.
II. By adding isoamyl iodide to diethylmethylamine.
III. By adding ethyl iodide to ethylmethylisoamylamine.

The platinichlorides of I, II and III gave on evaporation by means of heat needle-shaped crystals belonging to the *rhombic system.*

The platinichlorides of I and II on evaporation *in vacuo* gave needle-shaped crystals belonging to the *monoclinic system*, whilst III on evaporation under the same conditions gave needles which resembled those obtained by evaporation by heat.

Further the monoclinic needles on redissolving in hot water on evaporation were changed into the rhombic variety. They were also changed to the rhombic variety by adding excess of chlorhydric acid and allowing the solution to evaporate at the temperature of the atmosphere. From these results the author is led to the conclusion that *the difference in crystalline form is due to the various arrangements of the radicles ethyl, methyl, isoamyl and chlorine around the nitrogen atom, and, therefore, that stereo-isomers are possibly capable of existence in the case of quaternary ammonium compounds.*

22. "Acetylcarbinol (acetol), $CH_3{\cdot}CO{\cdot}CH_2{\cdot}OH$." By W. H. Perkin, Jun., Ph.D., F.R.S.

Some time since the author, in conjunction with Dr. Tingle (Proc., **73**, 156), succeeded in preparing acetylcarbinol by the hydro-

lysis of monochloracetone by means of barium carbonate. As, however, the amount obtained by this process is exceedingly small and its isolation extremely laborious, the author has been engaged for some time in endeavouring to improve the method of preparation. The following process was ultimately devised and employed with success in preparing large quantities of pure acetylcarbinol. 200 grams of acetylcarbinyl acetate, ($CH_3{\cdot}CO{\cdot}CH_2{\cdot}OC_2H_3O$), prepared by digesting monochloracetone with potassium acetate in alcoholic solution), is dissolved in 350 grams of water heated to boiling, and freshly precipitated barium carbonate added in small quantities at a time until no further action takes place. The clear solution is distilled as rapidly as possible under reduced pressure (100 mm.) and the distillate, which contains 20 per cent. of acetylcarbinol, very carefully fractionated under ordinary pressures with the aid of a long Glinsky column. After repeated fractionation a product is obtained which contains over 90 per cent. of acetylcarbinol. This is dissolved in pure ether, thoroughly dried with freshly ignited sodium sulphate, the ether distilled off and the residue fractionated under reduced pressure.

Acetylcarbinol boils at 120—122° under 250 mm., and at about 147° under ordinary pressure. When cooled in a mixture of ice and chlorhydric acid it solidifies to a hard, crystalline mass; its rel. den. at 15°/15° is 1·07915; its magnetic rotation 3·650.

Sodium amalgam converts acetylcarbinol quantitatively into *methylglycol*, $CH_3{\cdot}CH(OH){\cdot}CH_2OH$ (b. p. 188°).

23. "The action of ethyl dichloracetate on the sodium derivative of ethyl malonate." By Arthur W. Bishop, Ph.D., and W. H. Perkin, Jun., Ph.D., F.R.S.

When a mixture of ethyl malonate (2 mols.), sodium ethylate (2 mols.) and ethyl dichloracetate (1 mol.) is digested in alcoholic solution in a reflux apparatus, interaction rapidly takes place with separation of sodium chloride. At the end of two hours, the alcohol was distilled off, the residue mixed with water, extracted with ether and the oily residue which remains, after distilling off the ether, fractioned under reduced pressure. After repeated refractionation it was ultimately separated into two new compounds, *α-ethylic ethylenetricarboxylate*, $(CO_2Et)_2C{:}CH{\cdot}CO_2Et$, and *β-ethylic propanetricarboxylate*, $(CO_2Et)_2{:}CH{\cdot}CH(CO_2Et){:}CH(CO_2Et)_2$.

The former is a colourless, peculiar-smelling oil which boils at 203—205° (100 mm.); on hydrolysis, it yields ethylenetricarboxylic acid, and this, on heating to 180°, is decomposed quantitatively into *fumaric acid* and carbon dioxide.

The latter ethereal salt is an extremely thick oil which boils without decomposition at about 265° under a pressure of 80 mm. On hydrolysis it is converted into a polycarboxylic acid, probably propanepentacarboxylic acid, as the substance, when heated at 180°, readily loses carbon dioxide with formation of *tricarballylic acid*,

$$(COOH)_2{\cdot}CH{\cdot}CH(COOH){\cdot}CH(COOH)_2 = COOH{\cdot}CH_2{\cdot}CH(COOH){\cdot}CH_2COOH + 2CO_2.$$

24. "Benzoylacetic acid and some of its derivatives. Part V." By W. H. Perkin, Jun., Ph.D., F.R.S., and James Stenhouse.

This research was instituted with the object of supplementing and, in some cases, of rectifying the results obtained in investigations previously carried out on the same subject (compare Trans., **45**, 170; **47**, 240; **47**, 261; **49**, 154).

Ethylic benzoylacetate contains one hydrogen atom which is readily displaced by sodium, and the resulting sodium derivative yields, on treatment with alkyl iodides, the ethereal salts of higher homologues of benzoylacetic acid, of the formula $C_6H_5{\cdot}CO{\cdot}CHR{\cdot}COOC_2H_5$.

Sodium dissolves readily in ethereal solutions of these derivatives, but, in spite of a large number of experiments, no general method has as yet been found by which di-substituted derivatives of ethylic benzoylacetate (similar to those obtained from ethylic acetoacetate) can be prepared. When treated with sodium ethylate and alkyl iodides in the usual manner, mono-substituted derivatives of ethylic benzoylacetate usually yield only traces of di-substituted ethereal salts, $C_6H_5{\cdot}CO{\cdot}CRR'{\cdot}CO_2Et$, the greater portion being decomposed with formation of benzoic acid, fatty acids &c.

By digesting ethylic methylbenzoylacetate with sodium ethylate and allyl iodide in alcoholic solution in a reflux apparatus, however, an almost quantitative yield of *ethylic allylmethylbenzoylacetate*. $C_6H_5{\cdot}CO{\cdot}C(CH_3)(C_3H_5){\cdot}CO_2Et$, is obtained. This ethereal salt boils at 243—245° (225 mm.); on hydrolysis it yields quantities of benzoic acid, together with a small quantity of a ketone, probably allylmethylacetophenone.

Action of Hydroxylamine on Dibenzoylacetic Acid.—Dibenzoylacetic acid and hydroxylamine readily interact in alkaline solution, with formation of a substance, $C_9H_7NO_2$, which, on examination, was found to be identical with the *phenylisoxazolon*, $\begin{matrix} C_6H_5{\cdot}C{\cdot}CH_2{\cdot}CO \\ \| \quad\quad\quad | \\ N\text{——}O \end{matrix}$, obtained by Claisen (*Ber.*, **24**, 140) by the action of hydroxylamine on ethylic benzoylacetate. When heated with phenylhydrazine at 180°, ethylic dibenzoylacetate is completely decomposed with formation of *benzoylphenylhydrazine*, $C_6H_5{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}C_6H_5$. On reduction dibenzoyl-

acetic acid yields β-phenyllactic acid, $C_6H_5{\cdot}CH(OH){\cdot}CH_2COOH$, and *dihydroxydibenzoylacetic acid*, $[C_6H_5{\cdot}CH(OH)]_2{:}CH{\cdot}COOH$. This new acid crystallises from water in slender, glistening needles which melt at 188—190°.

Ethylic methyldibenzoylacetate, $(C_6H_5{\cdot}CO)_2{:}C(CH_3){\cdot}COOC_2H_5$, is prepared by the action of benzoyl chloride on the sodium compound of ethylic methylbenzoylacetate. It is a thick oil, which is much less stable than ethylic dibenzoylacetate and is almost entirely decomposed on hydrolysis with formation of quantities of benzoic acid.

Ethylic benzylbenzoylacetate, $C_6H_5{\cdot}CO{\cdot}CH(C_7H_7){\cdot}COOC_2H_5$, prepared by heating together ethylic benzoylacetate, sodium ethylate and benzyl chloride in alcoholic solution, is a thick, light-yellow oil boiling at 265° (80 mm.).

Benzylacetophenone, $C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5$, is obtained by the hydrolysis of the previous compound. It crystallises from alcohol in glistening plates which melt at 70°. It is converted by hydroxylamine into the hydroxime $C_6H_5{\cdot}C(NOH){\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5$, which melts at 80—81°. Reduction with sodium in moist ethereal solution converts benzylacetophenone into *diphenylpropyl alcohol*, $C_6H_5CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5$, a thick, colourless oil which boils at about 240° (70 mm.).

α-Methyl-β-phenyllactic acid, $C_6H_5{\cdot}CH(OH){\cdot}C(CH_3){\cdot}COOH$, obtained by reducing ethylic methylbenzoylacetate with sodium amalgam, melts at 95° (not at 124—125°, as previously stated, Trans., **49**, 160). When heated at 280°, it is decomposed with evolution of carbon dioxide and water and formation of methylstyrolene, $C_6H_5{\cdot}CH{:}CH{\cdot}CH_3$ (b. p. 174—175°).

α-Ethyl-β-phenyllactic acid, $C_6H_5{\cdot}CH(OH){\cdot}CH(C_2H_5){\cdot}COOH$, is obtained by the reduction of ethylic ethylbenzoylacetate with sodium amalgam. It crystallises from bisulphide of carbon in needles which melt about 108°.

Ethylic furfuralbenzoylacetate, $C_6H_5{\cdot}CO{\cdot}C(:CH{\cdot}C_4H_3O){\cdot}COOC_2H_5$, is prepared by heating a mixture of furfural, ethyl benzoylacetate and acetic anhydride at 180°. It crystallises from methyl alcohol in beautiful, glistening prisms which melt at 68°.

25. "Syntheses with the aid of ethyl pentanetetracarboxylate." (Preliminary note.) By W. H. Perkin, Jun., Ph.D., F.R.S., and Bertram Prentice.

Ethylic pentanetetracarboxylate (Trans., **51**, 241) yields a disodium derivative, $(COOC_2H_5)_2{:}CNa{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CNa{:}(COOC_2H_5)_2$, from which, by the action of alkyl iodides, higher homologues may be obtained, and these, on hydrolysis and subsequent splitting off of two molecules of carbon dioxide, yield higher homologues of pimelic acid,

$$(COOC_2H_5)_2{:}CR{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CR'{:}(COOC_2H_5)_2 + 4KOH =$$
$$(COOK)_2{:}CR{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CR'(COOK)_2 + 4C_2H_5OH.$$

$$(COOH)_2{:}CR{\cdot}CH_2{\cdot}CH_2CH_2{\cdot}CR'{:}(COOH)_2 =$$
$$COOH{\cdot}CHR{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHR'{\cdot}COOH + 2CO_2.$$

Ethylic dibenzylpentanetetracarboxylate,

$$(COOC_2H_5)_2{\cdot}C(C_7H_7){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}C(C_7H_7)(COOC_2H_5)_2,$$

prepared by the action of benzyl chloride on the disodium compound of ethyl pentanetetracarboxylate, is a solid, crystalline substance which melts at 75—77°.

Dibenzylpentanetetracarboxylic acid,

$$(COOH)_2{\cdot}C(C_7H_7){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}C(C_7H_7)(COOH)_2,$$

obtained by the hydrolysis of the above ethereal salt, is a colourless, crystalline substance, very sparingly soluble in ether. It decomposes at 207—210° into dibenzylpimelic acid and carbon dioxide. The silver salt, $C_{23}H_{20}Ag_4O_8$, is a white powder, insoluble in water.

Dibenzylpimelic acid,

$$COOH{\cdot}CH(C_7H_7){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(C_7H_7){\cdot}COOH,$$

crystallises from a mixture of benzene and light petroleum in well-formed, glistening prisms which melt at about 117°. The *barium salt*, $C_{21}H_{22}O_4Ba + 3H_2O$, is more soluble in cold than in hot water, and separates, when the cold saturated solution is heated to boiling, in colourless plates.

26. "The oxidation of mannitol by nitric acid. α-Mannosaccharic acid." By T. H. Easterfield.

The recent researches of Emil Fischer and his pupils have shown that, whereas mannose is almost quantitatively converted into mannitol on reduction, dextrose yields mannitol with difficulty: hence it appeared probable that dextrose and mannitol are not so directly related as has been supposed, and that as mannitol and mannose are easily converted, the one into the other, their relationship is a very close one; it therefore was to be supposed that mannitol, like mannose, would yield mannosaccharic and not saccharic acid, on oxidation with nitric acid. The author, at Professor Fischer's suggestion, has experimentally investigated this question, and his results completely confirm the correctness of the theoretical argument.

Mannosaccharic acid yields no sparingly soluble acid potassium salt; and it readily affords a double lactone.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE NEXT BALLOT.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

Bell, Albert, Edward,

Sherborne, Dorset.

Science Master at Sherborne School. Received chemical education at Owens College, during the years 1884, 1885, 1886, taking 3rd place in Senior Chemistry Examination at the Normal School of Science, 1886, 1887; assisted Dr. Percy Frankland in original work on the Estimation of Nitrogen; 1st Class Honours Practical Inorganic Chemistry; Science Master at Sherborne Grammar School since 1888.

T. E. Thorpe.	Alfred E. Tutton.	Percy F. Frankland.
Watson Smith.	E. P. Perman.	*Chapman Jones.*
	W. P. Wynne.	

Bater, Claude Hooper,

4, Westbank Terrace, Gibson Street, Hillhead, Glasgow.

Chemical Officer, Inland Revenue. Student in Theoretical Chemistry at the Royal School of Mines, under Professors Frankland and Japp, 1884–5, and in Practical Chemistry at the Inland Revenue Laboratory, Somerset House, during same period; taking 1st Class Certificate at end of the course. Two years' experience in analytical work in Somerset House Laboratory, 1885–7, followed by $3\frac{1}{2}$ years' experience as a Chemical Officer of Inland Revenue at Glasgow Inland Revenue Laboratory.

Richard Bannister.	Wm. Harkness.	H. J. Helm.
J. R. Jackson.	E. Grant Hooper.	C. Proctor.

Barnes, Edward Arthur,

57, Delafield Road, Charlton, S.E.

Chemist. Associate of the City and Guilds of London Institute.

Analytical Chemist at Abram Lyle & Co.'s Sugar Refinery, Silvertown.

Henry E. Armstrong. W. P. Wynne.
Gerald T. Moody. Harold G. Colman.
Holland Crompton. Henry A. Miers.
G. H. Robertson.

Bate, William,

National Explosives Co., Hayle, Cornwall.

Five years Assistant, and five years Chemist, to the St. Helen's Chemical Co., St. Helen's, Lancashire; at present Chemist to the National Explosives Co., Hayle, Cornwall.

George Lunge. Arnold Philip.
P. Gerald Sanford. Alfred C. Fryer.
John J. Beringer. *F. E. Matthews.*
William Newton. *C. Heinrich Trinks.*
P. Coulson Bunn.

Rhys, Pendrilt Charles,

Plas Newydd, Neath.

Analytical Chemist. One year at the City and Guilds of London Central Institute, three years as Student with Dr. Morgan, Ph.D., Public Analyst for Swansea, Glamorgan, &c.; now Assistant Chemist at the Swansea Hematite Iron Co., Landore, South Wales.

Wm. Morgan, Ph.D. Frank B. Last. Herbert Eccles.
H. M. Faber, M.A., Ox. *W. Terrill.* *T. Redwood.*

Cooper, Walter Johnson,

High Street, Mitcheldean, Glos.

Portland Cement Works Manager, and Analytical Chemist. Nine to ten years student of Chemistry and General Science; 6½ years Analytical and Research Chemist in Portland Cement Works, the last 2½ years Manager also.

John Cuthbert Welch. Alfred J. Shilton.
Alfred C. Fryer, Ph.D., M.A. Walter F. Reid, F.I.C.
C. W. Stephens.

Evans, Frederick Arthur,

O'okiep, Cape Colony, South Africa.

Manager of Copper Smelting Works. Served articles with Dr. William Morris, Public Analyst, Swansea; Chemist to the Cape Copper Co., Natal, superintending manufacture of copper, at Cape Copper Co.'s Mines, South Africa.

Wm. Morgan, Ph.D. Jas. S. Merry.
W. Terrill. Alfred H. Knight.
Leonard Temple Thorne. *Bertram Blount.*

Fowler, Gilbert John,

Dalton Hall, Victoria Park, Manchester.

Assistant Demonstrator in the Chemical Laboratories, Owens College. Master of Science, Victoria University, 1st Class Honours in Chemistry; joint author of papers on:—"Suboxide of Silver," "Some Reactions of the Halogen Acids," "On the Influence of different Oxides on the Decomposition of Potassium Chlorate."

C. Schorlemmer. Harold B. Dixon. G. H. Bailey.
J. B. Cohen. P. J. Hartog. Gibson Dyson.

Fitze, Joseph,

1, New China Bazaar Street, Calcutta.

Assistant Chemist to D. Waldie & Co., of Cossipore Chemical Works, Calcutta. Two years student at the Royal School of Mines, South Kensington. Three months in laboratory of Messrs. Lawes' Chemical Manure Works.

T. E. Thorpe. F. R. Japp. Wm. Tate.
W. R. Criper. *J. H. Wilson.* *John Hughes.*

Foster, John Alfred,

Royal Naval College, Greenwich, S.E.

Analytical Chemist. Assistant to Prof. V. B. Lewes, Royal Naval College, and late assistant and student with A. Norman Tate, Esq., F.I.C., &c., Liverpool.

Vivian B. Lewes. W. Popplewell Bloxam, B.Sc.
A. Norman Tate. *John M. Thomson.*
G. Stillingfleet Johnson.

Forshaw, Chas. F., LL.D., D.Sc., Ph.D.,

Bradford, Yorks.

Doctor of Dental Surgery. Author of "Alcohol: its Use and Abuse," "Tobacco and its Effect on the General Health," each of which is printed, the above subjects having formed themes for a lecture, which the author has delivered to different societies in Bradford and elsewhere; also of numerous works on "Poetry," &c., &c., F.R.M.S., F.G.S. Edin., &c., &c., late F.S.C.I.

Rev. H. Ross, B.Sc., Hon. LL.D. Robert Galloway.
Fredk. Woodward Branson. *I. Patchett.*
George H. Hurst. *Jas. Baynes.*

Greaves, J. A. R.,

Old Rectory, Grappenhall, Cheshire

Brewer. Practically connected with chemistry all my life, 1st in medicine; 2ndly, in architecture: 3rdly, as brewer and maltster,

having studied it for the last 20 years in connection with the latter; also studied biology for the last 20 years.

Thos. Fletcher. Horace T. Brown. W. S. Squire.
Walter Odling. *Charles Graham.*

Gibbins, Berington H.,

Ocala, Florida, U.S.A.

Technical Chemist. Received chemical education at Owens College; 4 years Chemist at Melincrythan Chemical Works, Neath; 6½ years in charge of sulphuric acid and superphosphate plants of J. L. Morgan & Co., New York.

J. H. M. Fallon. H. E. Roscoe. Chas. J. Waterfall.
John Ruffle. *Bernard Dyer.* *F. H. Perry Coste.*
Frank L. Teed. *Charles E. Cassal.* *Otto Hehner.*

Hiepe, William L., Ph.D.,

21, Acomb Street, Manchester.

Analytical Chemist, 19, Kilvert's Buildings, Withy Grove, Manchester. Ph.D. of Berne, Switzerland. Eight years assistant to Dr. Hill, Birmingham; 4 years in charge of laboratory of Mr. Frank Faulkner; 2½ years independently.

Louis Siebold. Alfred Hill. Basil Pemdarne Wigan.
Otto Hehner. *Bernard Dyer.* *Charles E. Cassal.*

Hart, William Beamont,

Gransmoor Avenue, Fairfield, near Manchester.

Fellow of the Institute of Chemistry, Ordinary Member of the Berlin Chemical Society. Papers:—"Volumetric Method of Antimony Estimation" (*Jour. Soc. Chem. Ind.*, 3, 294); "Investigation of an Alleged Reaction for Sodium Carbonate Manufacture" (in conjunction with Watson Smith, Esq., F.I.C., F.C.S.) (*Jour. Soc. Chem. Ind.*, 5, 643); "On some Organo-Silicon Compounds," British Association, 1887. Research Chemist at the Clayton Aniline Company, Limited, Clayton, near Manchester.

Henry E. Roscoe. Watson Smith. G. H. Bailey.
C. Schorlemmer. Harold B. Dixon. Arthur Harden.
J. Carter Bell.

Joseland, Walter Herbert,

9, Campbell Grove, Oxford Road, Manchester.

Assistant in Dr. E. Schunck's Laboratory. Studied Chemistry 3½ years at the Owens College, Manchester. Obtained degree of B.Sc. (1st Class Honours, Chemistry) Victoria University, June, 1890. Associate Instit. of Chemistry, July, 1890.

C. Schorlemmer. Harold B. Dixon. G. H. Bailey
J. B. Cohen. Jas. Grant. *Francis Jones.*

Kipping, F. Stanley, D.Sc. (Lond.).

7, Milborne Grove, South Kensington.

Lecturer and Assistant in the Chemical Research Laboratory, City Guilds of London, Central Institution. Three papers communicated to the Chemical Society by myself. Five papers, ditto, conjointly with Professor W. H. Perkin, jun. One paper, ditto, conjointly with J. E. Mackenzie, B.Sc.

Henry E. Armstrong. W. H. Perkin. T. E. Thorpe.
Charles E. Groves. W. H. Perkin, jun.

Lauder, Alexander,

Bangor, North Wales.

Chemist, University College of North Wales, Bangor. Studied Chemistry, first at Greenock, for two years under J. W. Biggart, Esq., Public Analyst there, and Angus Smith, Esq., F.C.S., &c.; then for a year under Professor Dittmar, in Glasgow. For the last year and a half has been private assistant to Professor Dobbie, University College of North Wales, Bangor, assisting him in various researches, &c.

James J. Dobbie. George McGowan. John Wm Biggart.
John Ferguson. *G. G. Henderson.* *Edmund J. Mills.*

Langham, Rev. Edgar Norman, M.A., St. John's College, Cambridge.

7, Claremont, Ripon.

Science Master (five years Teacher of Chemistry), Ripon Grammar School. Before University Course:—First Class Elementary and Advanced Certificates in Chemistry (Science and Art Department). At Cambridge:—studied Theoretical Chemistry; also Practical Chemistry in the College Laboratory; and attended the lectures of the College Lecturer and University Professor. After University Course:—Science Master, Ripon School, since December, 1885, Chemistry being leading subject. Have pased many pupils in Elementary and Advanced Science Department Examinations in Theoretical and Practical Work; also in Senior and Junior Cambridge Local Examinations, having obtained the mark of distinction.

Fredk. W. Boam, F.G.S. Fredk. Woodward Branson, F.I.C.
Geo. W. Slatter. A.R.C.S., F.I.C. *J. G. F. Richardson.*
Sydney Lupton. *Richard Reynolds.* *R. Hayton Davis.*
A. Humboldt Sexton.

Leicester, James,

2, Queen's Parade, Brandon Hill, Bristol.

Lecturer on Chemistry and Metallurgy, Merchant Venturers' School, Bristol. Ph.D. of the University of Erlangen. Author of

"The Action of Quinones on o-Diamines and o-Nitroaniline and Nitroparatoluidine" (*Ber.*, **23**, 2793—2798).

J. Campbell Brown. Charles A. Kohn. Arthur Richardson.
J. Bishop Tingle. W. Johnston Saint.

Morrison, Geo. R.,

Richmond House, Plaistow.

Manager and Consulting Chemist to Jeyes Sanitary Compounds Company, Limited, Plaistow. Studied, theoretically and practically, Chemistry, five years; Natural Philsophy, two years; Geology, two years; Mathematics, two years, at Glasgow University. Was Manager and Chemist for some years at the Chemical Works of the Glasgow Corporation Gas Works.

Robert R. Tatlock. John Ferguson. William Ramsay.
James Mackey. *J. Falconer King.* *John B. Orr.*

MacDonald, William,

109, Crofton Road, Peckham, S.E.

Assistant Chemist, Riotinto Copper Company. Studied four years at the Royal School of Mines and College of Science, London. Associate in Chemistry, R.C.S., in Metallurgy, R.S.M., and of the Institute of Chemistry, G.B. and I.

W. R. Hopkinson. T. E. Thorpe. W. C. Roberts-Austen.
Chapman Jones. Alfred E. Tutton. William Tate.

Mitchell, Charles Ainsworth,

27, Farnley Road, South Norwood, S.E.

Scholastic. Student (formerly) at the University Laboratory, Oxford. B.A. final in Chemistry, Practical and Theoretical, 1888. Preliminary Honour Chem. (Practical and Theoretical) 1889. Till Christmas, 1890, Assistant Chemical Master at King William's College, Isle of Man.

W. W. Fisher. V. H. Veley. W. Odling.
J. E. Marsh. *John Watts.*

Merrils, Frederick Johnson,

65, Roe Lane, Pitsmoor, Sheffield.

Analytical Chemist. Five years Manager, and three years Chemist, at the Sheffield United Gas Light Company's Sulphuric Acid and Sulphate of Ammonia Works. Chief Assisiant in J. O. Arnold's Metallurgical Laboratory. Evening Demonstrator in Metallurgy at the Sheffield Technical School.

J. O. Arnold. B. W. Winder. Edward Jackson.
L. Napier Ledingham. John C. Platts.
Thos. Andrews. *Charles Bradshaw.*

Ough, Lewis,

15, Upper King Street, Leicester.

Laboratory Manager and Analyst for J. Richardson and Co., Manufacturing Chemists, Leicester. A Student for Session 1888 at the School of Pharmacy of the Pharmaceutical Society of Great Britain, under Professor J. Attfield, F.R.S., Ph.D., Professor W. R. Dunstan, M.A., Professor J. R. Green, B.A., E. M. Holmes, Esq., F.L.S., and J. Ince, Esq., and at the competitive examinations at the end of the course on the recommendations of the above professors and teachers, obtained first place in all the subjects, viz.:—Practical Chemistry, Theoretical Chemistry, Botany, Materia Medica, and Pharmacy, and was awarded a medal in each case. Was awarded the Bronze Medal of the Pharmaceutical Society for distinguished merit in the Council Examination Prizes 1889. A worker for five months in the Research Laboratory of the Pharmaceutical Society, under Professor W. R. Dunstan, M.A., and an assistant for sixteen months with S. W. Rich, Esq., F.I.C., Commercial Analyst, Croydon.

Jno. Geo. Fred. Richardson. Wyndham R. Dunstan.
John Attfield. M. Carteighe. *Alonzo J. Rider.*
Hubert N. B. Richardson.

Randall, Percy Morrice,

3, Belsize Park Gardens, N.W.

Chemist to the firm of Randall Bros. Has studied Chemistry at the Royal College of Science, South Kensington, and at King's College, London.

T. E. Thorpe. Alfred E. Tutton. John M. Thomson.
G. Stillingfleet Johnson. *Chapman Jones.* *William Tate.*

Storey, James Ashburner,

Moorside, Lancaster.

Chemical Manufacturer. Four years a student in the Chemical Laboratories of the Owens College. B.Sc. with Honours in Chemistry, Victoria University. Associate of the Institute of Chemistry, 1890.

Harold B. Dixon. G. H. Bailey. J. B. Cohen.
P. J. Hartog. Gibson Dyson.

Searl, Albert,

The Caxtons, Miskin Road, Dartford.

Manager, Phœnix Mills, Dartford (Messrs. Burroughs, Wellcome & Co.). Fifteen years' experience in analytical work in laboratory of Messrs. Howards & Sons, City Mills, Stratford; improvements in

Pharmaceutical preparations, as regards purity, detection of impurities and use of bye-products.

David Howard. Alfred G. Howard. D. Lloyd Howard.
John Hodgkin. J. Hersee Freeman. *Alfred Hy. Mason.*
Chas. W. Vincent.

Tocher, James Fowler,

1, Chapel Street, Peterhead.

Pharmaceutical Chemist, in business with Analytical Practice. Associate of the Institute of Chemistry (Exam.). Author of Papers:—"Analysis of Waters of the Springs and Wells of Peterhead," *Trans. Buchan Field Club*, 1889; "Tests for Detection of Sesame Oil in Olive Oil," "Isolation of another substance from Sesame Oil," *Jour. Phar. Soc.*, January, 1891.

William A. Tilden. Thomas Turner. W. W. J. Nicol.
Charles R. Beck. J. J. Sudborough. *M. Carteighe.*
F. R. Japp.

Thonger, Cecil Geo. Freer, M.R.A.C.,

Colonial College, Hollesley Bay, Suffolk.

Late Professor of Agriculture and Chemistry, Texas University, U.S.A., at present Professor of Agriculture and Chemistry, Colonial College, Hollesley Bay. Studied Agricultural Chemistry and Analysis, for 3 years at the Royal Agricultural College, Cirencester, of which I hold the Diploma and Gold Medal, also Diploma and Special First Class Certificate of the Royal Agricultural Society of Ireland, and intend to pursue the study of Agricultural Chemistry. Professor of Agriculture and Agricultural Chemistry, Colonial College, Hollesley Bay.

Edward Kinch. H. H. Robinson. R. Warington.
Robert Wallace. *John Hunter.*

John Wild,

28, Hyde Road, Woodley, Stockport.

Research Student. Three years' study of Chemistry in the Owens College. B.Sc., Victoria University. Associate of Inst. of Chemistry. July, 1890.

C. Schlorlemmer. Harold B. Dixon. G. H. Bailey.
J. B. Cohen. Francis Jones. Jas. Grant.

HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY, ST. MARTIN'S LANE.

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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 96. Session 1891-92.

March 25th, 1891. Annual General Meeting. Dr. Russell, F.R.S., President, in the Chair.

The President delivered an address, of which the following is an abstract:—

The number of Fellows is 1786, of whom 32 are honorary foreign members. One foreign member, Dr. Heinrich Will, and 17 Fellows have died during the year:—Dr. M. Bechler, W. Blythe, H. B. Brady, F.R.S., C. I. Burton, W. Lant Carpenter, Prof. T. Carnelley, J. B. Hutcheson, J. A. Hill, Robert MacCalmont, E. C. Nicholson, T. R. Ogilvie, C. P. Phillips, H. Poland, H. Smith, W. C. Stevens, F. O. Landell and H. H. Walker.

The following 13 Fellows have withdrawn:—A. Bain, E. N. Butt, J. Barker, R. Carruthers, W. H. Glazier, J. Hall, A. E. Johnson, E. A. Parnell, W. E. Porter, W. R. Reffell, J. Stokes, A. Taylor, and R. C. Tresider.

28 Fellows have been removed from the list on account of arrears:—B. Akroyd, H. J. Alford, P. H. Cathcart, F. W. Dupré, A. F. Darnon, H. Eccles, W. T. Elliott, J. W. Ellis, M. P. Gosset, E. Ernest Graves, T. F. Garwin, T. Hart, W. H. Hyatt, F. H. Lowe, H. A. B. Leipner, T. Muskett, F. Nettlefold, C. O'Keefe, L. Peckitt, G. F. Rodwell, V. P. Richards, A. H. F. Ruppell, A. E. Simpson, W. F. K. Stock, C. A. Smith, P. C. Thomas, Dr. W. H. Wilson and W. A. Wren.

114 Fellows have been elected during the year, being 31 fewer than last year.

The financial state of the Society is not quite so satisfactory, said the President, as it has been for some years past, the receipts from subscriptions being £177 less than last year. This falling off is to be

accounted for, partly by the accidental circumstance that there were 11 fewer life compositions than last year, but chiefly by the fact that no fewer than 26 candidates had been blackballed.

The same number of papers, viz. 72, have been printed in the Transactions as last year, but they occupy no fewer than 1051 pages, instead of 772 pages in the previous year. There has been a considerable increase in the number of abstracts, 2341 appearing this year, and occupying 1527 pages, whereas last year the number was 2131, which occupied 1252 pages. Hence the cost of the Journal has been greater this year by £413.

All the new and valuable works on chemistry have been added to the Library as they were published.

The time had again come round for the award of the Longstaff medal, given every third year to the Fellow of the Society who, in the opinion of the Council, had done the most to promote chemical science by research. This instruction was not always easy to carry out; but the unanimous decision arrived at on this occasion to award the medal to Professor Japp would certainly, he thought, be regarded by the Fellows generally as eminently satisfactory. All who followed the higher development of organic chemistry knew how valuable were the carefully thought-out papers which Professor Japp had communicated to the Society. It was a matter of regret that he was unavoidably prevented attending the meeting to receive the medal in person.

The great event of the year had undoubtedly been the celebration of the Jubilee on February 24th and 25th; it was the intention of the Council to issue in a separate form a full account of the proceedings on these occasions. With reference to the reception held at Goldsmiths' Hall on the evening of the 24th by the President and Council, the Goldsmiths' Company had not only lent their Hall for the occasion, but with that liberality for which the great City Companies were so noted, "recognising that the occasion was of quite an exceptional character," had expressed their wish to relieve the Society from the expense attending the preparation and use of the Hall.

The suggestion made in his previous address that a subject catalogue of the Journal from its commencement might be published as a fit memorial of the Jubilee had, he thought rightly, been abandoned, as it appeared that the labour and expense involved would be greater than the result would justify.

It seemed appropriate to the occasion to briefly chronicle the changes which had occurred in the constitution and government of the Society since its foundation. Little or no alteration of bye-laws or plan of working the Society occurred during the early years. In 1852 the number of Vice-Presidents, which was then four, was increased by adding all past Presidents; but it was not until 1866

that any other change worth recording took place. In that year a new form of nomination paper was introduced, and this seems to be the first indication of any feeling having arisen that undesirable people were seeking and obtaining admission into the Society: this question had from time to time caused more discussion among the Fellows than any other relating to the government of the Society.

As chemistry became of more public importance, a very natural impression gained ground that, since all the more distinguished chemists of the day belonged to the Society, therefore every Fellow must be a thorough chemist. This misconception on the part of the public had had a most mischievous effect. In 1867 the matter was very fully discussed, and was ultimately referred by the Council to a committee consisting of Mr. Crookes, Dr. Miller, Dr. Odling, Mr. Wanklyn and Dr. Williamson. The report of this committee was adopted and sent to all the Fellows, and it stated the case so fully that it appeared well to republish it on the present occasion. This committee decided not to recommend "any alteration in the bye-law relating to the election of Fellows which would have the effect of confining the Fellowship of the Society to strictly scientific men." But with a view to increase the security against the election of undesirable candidates, they recommended that the number of signatures attached to a certificate be five instead of three, three instead of one to be from personal knowledge. The recommendations were adopted, and appear to have met the requirements of the case, as the agitation ceased.

In 1877, another similar outbreak took place, but on this occasion the feeling that it was practically impossible for the Society to insist on all its Fellows being trained and competent chemists became so strong that ultimately it was decided to found the present Institute of Chemistry.

Now, after the lapse of 14 years, a discussion is again raised, but the collateral circumstances are very different, as, through the existence of the Institute, all who desire to be stamped as educated chemists have the opportunity of obtaining such recognition. It was, however, necessary to arrive at a clear understanding as to who we desire to attract, and who we desire to exclude from our Society. Speaking for himself, said the President, he should wish to see the entrance made easy for all who have any real interest in our science, even if they be only amateur chemists, provided that socially there be no objection to their admission; he would entirely abandon the idea that amount of chemical knowledge is to determine the suitability of a candidate.

It was practically impossible by any hard-and-fast rules to exclude undesirable persons, and the history of the Society went to show that

the only effective method was for the Fellows themselves to realise that it rested with them to recommend only proper persons.

What had been the history of the Society during the past 14 years as showing whether the means at disposal had been effective in securing the prosperity of the Society? Without a shadow of doubt, the Society never stood so high both in the scientific and external world as at the present time; his experience during the past two years had shown him how widely the Society was known, and in how favourable a light it is regarded at home and abroad.

If the feeling be cultivated and generally acknowledged that the body of Fellows expect and require that all should act honestly and honourably towards one another, there will be very few improper persons gaining admission. On learning that any Fellow is acting in any way wrongly or dishonourably towards the Society, the first thing in future will be to ascertain, by reference to the Proceedings, who are the five Fellows who certified that the said Fellow was a proper person to join the Society. Nothing is more powerful than public opinion, and if it be felt that such a spirit should guide all elections, far more good will accrue to the Society than any law can effect which can be invented or enforced.

Dr. Gilbert proposed a vote of thanks to the President, coupled with the request that he allow his address to be printed; the motion was seconded by Mr. Carteighe Both speakers referred in most appreciative terms to Dr. Russell's services to the Society, especially on the occasion of the Jubilee celebration. Dr. Teed supported the motion, which was carried by acclamation. The President having acknowledged the vote,

Professor Thorpe, the Treasurer, gave an account of the financial position of the Society. The receipts from Fellows had been £3459 16*s.* 0*d.*; from sale of the Journal £383 9*s.* 4*d.*; and by dividends on invested capital £363 0*s.* 6*d.* The expenses on account of the Journal had been £2724 0*s.* 10*d.*; on account of the Library £300 18*s.* 9*d.*; on account of the Proceedings £183 7*s.* 10*d.*—the total expenditure being £3790 4*s.* 9*d.* The balance at the bank was £1798 17*s.* 7*d.*; and £600 had been invested in Metropolitan Board of Works $3\frac{1}{2}$ per cent. stock.

Professor Attfield proposed that the thanks of the Fellows be tendered to the Treasurer. Dr. Atkinson, in seconding the vote, lamented the loss of income during the year, and referred to the smaller expenditure out of the Research Fund, and the excessive balance at the bank.

Dr. Stevenson advocated a larger expenditure on the Library. Mr. Friswell followed Dr. Atkinson in lamenting the diminution in income

and its cause, and also referred to the disproportion borne by the life composition fee to the annual subscription. Mr. Cassall asked that increased facilities of using the Library might be granted to Fellows.

The President said that every effort was made by the Library Committee to obtain books, and that if Dr. Stevenson and others who complained of deficiencies would point out what was required, the Library Committee would most certainly pay the utmost attention to their recommendations. The Library would be open at any reasonable and rational time.

[Dr. Thorne subsequently stated that the statistics of attendance on evenings other than those when meetings took place in the buildings were such as to indicate that there was no great desire to use the Library in the evenings.]

It so happened that a considerable sum had been voted out of the Research Fund at a time just outside the financial year, so that actually the expenditure was greater than appeared.

The Treasurer, in acknowledging the vote of thanks, said that the large balance would very soon disappear, as a number of heavy payments had to be made. He took occasion to gratefully acknowledge the service which Mr. Tutton had rendered him in keeping the Society's accounts, and finally proposed that thanks be given to the Auditors, Messrs. H. Crompton, R. H. Davies and B. Dyer. This proposal was seconded by Dr. Collie and adopted. Mr. Dyer having replied.

Professor Ramsay moved a vote of thanks to the Officers and Council, which was seconded by Mr. Friswell, and acknowledged by Dr. Armstrong.

Mr. Warington finally proposed that thanks be tendered to the Editor, Sub-Editor, Abstractors and Librarian. Dr. Clowes seconded the motion. Mr. Groves and Dr. Thorne replied.

Scrutators having been appointed, a ballot was taken, and as result the following were declared elected as Officers and Council for the ensuing session.

President: Dr. A. Crum Brown, F.R.S.

Vice-Presidents who have filled the office of President: Sir F. A. Abel, K.C.B., D.C.L., F.R.S.; W. Crookes, F.R.S.; E. Frankland, D.C.L., F.R.S.; J. H. Gilbert, Ph.D., F.R.S.; J. H. Gladstone, Ph.D., F.R.S.; A. W. Hofmann, D.C.L., F.R.S.; H. Müller, Ph.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, Ph.D., F.R.S.; Sir Lyon Playfair, Ph.D., K.C.B., F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents: G. Carey Foster, F.R.S.; W. N. Hartley, F.R.S.; John Pattinson; J. Emerson Reynolds, M.D., F.R.S.; William A. Tilden, F.R.S.; Robert Warington, F.R.S.

Secretaries: H. E. Armstrong, Ph.D., F.R.S.; J. Millar Thomson, F.R.S.E.

Foreign Secretary: Raphael Meldola, F.R.S.

Treasurer: T. E. Thorpe, B.Sc., F.R.S.

Ordinary Members of Council: E. Atkinson, Ph.D.; Henry Bassett; Norman Collie, Ph.D.; John Ferguson, M.A.; E. Kinch; M. M. P. Muir; F. J. M. Page; W. H. Perkin, jun., F.R.S.; S. U. Pickering, M.A.; Boverton Redwood; Thomas Purdie, B.Sc.; John A. Voelcker, Ph.D.

The meeting then proceeded to consider the alterations in the bye-laws proposed by the Council. The first alteration having been read to the meeting,

Mr. Lloyd asked the President what would be his ruling with reference to any new proposal made at the meeting to alter the bye-laws.

The President said that he could not allow any proposal to alter the bye-laws of which notice had not previously been given to the Fellows to be put at that meeting. Although there was no express provision to that effect either in the charter or bye-laws, it was manifestly inexpedient to adopt any other course, and such ruling would be in accordance with the practice of the Society hitherto.

Mr. Lloyd stated that the movement in which he and others had taken part had for its object to exclude those who were personally objectionable, and to effect this they desired to place the nomination of Fellows in the hands of the Council. He therefore moved as an amendment that the whole subject of the alterations in bye-laws be postponed.

The President having ruled this amendment out of order, after a few remarks from other speakers, a vote was taken, and the following alteration in the bye-laws was carried, there being only five dissentients.

> "That in the case of candidates resident abroad unable to obtain the before-mentioned number [five] of signatures, the Council shall have power to accept a certificate, signed from personal knowledge by one Fellow of the Society, and to recommend its presentation for ballot."

Subsequently the following were also put to the meeting and carried all but unanimously.

2. That the following notice be printed at the head of the Form of Recommendation:—

> "The attention of the candidate in whose favour this certificate is

made out is specially directed to the fact that, if elected, he wil be required to sign the following obligation prior to his admission into the Society :—

"Obligation.—I, the undersigned, do hereby engage that I will endeavour to promote the interests and welfare of the Chemical Society, that I will observe its laws, and to the utmost of my power maintain its dignity, as long as I shall continue a Fellow thereof.

3. That Bye-law XII be altered so that it read as follows :—

"An Annual General Meeting of the Society shall be held on the 30th day of March, or on some day in March near that time, and at such an hour as the Council may determine, for the election of Officers, &c."

April 2nd, 1891. Mr. W. Crookes, F.R.S., Vice-President, in the Chair.

Certificates were read for the first time in favour of T. St. John Belbin, 12, Bolton Mansions, South Kensington ; James Lane Notter, Leigh Grange, Woolstone, Southampton; Frederick Tetley, 3, Mannville Terrace, Horton Road, Bradford.

The following papers were read:—

1. "Citraconfluorescein." By J. T. Hewitt, B.A., B.Sc.

With the object of further comparing citraconic with maleic anhydride, the latter having been shown by Lunge and Burckhardt to be capable of yielding a fluorescein, the author has submitted citraconic anhydride to the action of resorcinol in presence of sulphuric acid, and finds that, like maleic anhydride, it yields the corresponding fluorescein. Citraconfluorescein is readily soluble in alcohol and glacial acetic acid, and fairly soluble in water; the aqueous solution is of a yellowish-brown colour, and exhibits a green fluorescence less vivid than that of ordinary fluorescein.

2. "Ethylic thiacetacetate." By C. T. Sprague, B.Sc., Ph.D.

The author describes a series of experiments made with the object of determining the constitution of the ethylic thiacetacetate which Hübner obtained by the action of sulphur monochloride, S_2Cl_2, on ethylic acetacetate, and which, after his death, was studied by Buchka. The same substance has since been prepared by Deliole by

the action of sulphur dichloride, SCl_2, on ethylic acetacetate; by Schönbrodt by the action of sulphur on the copper derivative of ethylic acetacetate; and by Michaelis and Phillips from thionyl chloride and ethylic acetacetate. Buchka proposed the formula $S(CH{\cdot}Ac{\cdot}CO_2Et)_2$, but an alternative formula $S(O{\cdot}C{:}CH{\cdot}CO_2Et)_2$ was suggested by Deliole.

After describing the preparation of the substance, the author discusses the discrepant statements made by different observers as to its melting point. He then describes at length the products of the interaction of hydrazines and ethylic thiacetacetate, and shows that it behaves towards phenylhydrazine, &c., in the same manner as ethylic acetacetate: in the first instance, a pyrazolone sulphide is formed from two molecules of the hydrazine and one of the thiacetate; the sulphides are in the next instance converted by further action of the hydrazine into pyrazolone disulphides and bisphenylmethylpyrazolone or the homologous substances; and, finally, the pyrazolone disulphides and the hydrazine interact to form hydrogen sulphide and hydrazones of the pyrazole series. The results afford further proof of the correctness of Buchka's formula.

3. "The function of chlorine in acid chlorides as exemplified by sulphuryl chloride." By Henry E. Armstrong.

A large number of experiments carried out during recent years in the author's laboratory show that sulphuryl chloride, SO_2Cl_2, acts on benzenoid compounds, if at all, uniformly in the remarkable manner first pointed out in the case of phenol by Dubois in 1867 (*Zeits. f. Chemie*, p. 705), and in several other cases by subsequent observers, *simply as a chlorinating agent.* Sulphuryl chloride is in many respects a remarkable compound: it is very easily produced by the direct union of sulphur dioxide and chlorine in presence of a catalyst, such as camphor, charcoal or acetic acid, but little heat being evolved in its formation; it is a highly mobile liquid of low boiling point; and it is acted on with extreme slowness by water and alkaline solutions. It is, in fact, a surprisingly inert substance, possessed of properties by no means such as are usually regarded as characteristic of acid chlorides. The author questions whether after all the chlorine in acid chlorides is possessed of special activity. Probably our ideas on the subject are based too much on the consideration of the properties of the most familiar of acid chlorides, acetic or acetyl chloride; benzoic chloride, it is well known, is a far less active substance, and many other acid chlorides are but slowly attacked by water. It would appear that in sulphuryl chloride the chlorine is but loosely held, and that it is easily withdrawn by a compound having an affinity

for chlorine: naphthalene, for example. On slightly warming a mixture of this hydrocarbon and sulphuryl chloride, SO_2 is at once evolved, and the naphthalene is rapidly converted into tetrachloride. The SO_2 radicle in the chloride being all but destitute of "residnal affinity," the compound has but little tendency to act as a whole. The view that the activity of acid chlorides is conditioned by the oxygen rather than the chlorine is strongly supported by Wagner and Saytzeff's observations, and the later ones of Pawlow (*Annalen*, **188**, 104) on the action of zinc organometallic compounds on acid chlorides, which, there can be little doubt, attack the oxygen and not the chlorine: $R{\cdot}COCl + ZnMe_2 = R{\cdot}CMeCl(O{\cdot}ZnMe)$.

Perhaps also the activity even of so powerful an agent as chlorosulphonic acid, SO_3HCl, should be ascribed less to the chlorine than to the oxygenated radicle; this view is borne out by the fact that the analogous compound SO_3EtCl is a very inert substance. Both these compounds act, in the main, as sulphonating agents, and may perhaps be regarded as mere forms of SO_3. It would almost seem that on very slight provocation they become resolved into SO_3 and either HCl or EtCl, and that in the case of SO_3HCl the formation of acid chloride (sulphochloride), which is so frequently observed, is effected indirectly by the conjoint action of hydrogen chloride and SO_3, an interaction taking place analogous to that by which acetic chloride is formed by the conjoint action of hydrogen chloride and phosphoric anhydride on acetic acid.

Pyrosulphuryl chloride, $S_2O_5Cl_2$, which is an extremely active substance, although not rapidly acted on by water, also acts as a chlorinating agent, behaving much as if it consisted of SO_3 and SO_2Cl_2; in some cases it gives rise to the formation of a very large proportion of sulphochloride, which probably is a direct product of its action. There is no reason to suppose, however, that even in this chloride the chlorine is specially active.

A detailed description will be given later on of a long series of observations on the action of the various sulphuryl compounds above referred to.

4. "The action of nitric acid on the ligno-celluloses." By C. F. Cross and E. J. Bevan.

Dilute nitric acid attacks the ligno-celluloses when heated with them at 60°. The products are in the first instance a bright yellow derivative of the fibre substance (lignone) and nitrous acid. By the further interaction of these, a characteristic decomposition is determined, large quantities of nitrous oxide (N_2O) being evolved together with carbonic anhydride, only a small proportion of nitric oxide

being formed. A sensible quantity of hydrogen cyanide is also produced, the proportion being increased by increase of temperature.

These observations point to the entrance of the NOH residue into the lignone molecule and its interaction with nitrous acid according to the equation $\overset{|}{\underset{|}{C}}\!:\!NOH + NOH{\cdot}O = N_2O + H_2O + \overset{|}{\underset{|}{CO}}$, the final result being the displacement of 2H by O. The action is probably general for compounds containing the NOH residue—hydroximes and nitrolic acids—and the authors suggest that attention should be paid to the gaseous products formed by the interaction of nitric acid and carbon compounds as calculated to elucidate their mechanism.

The investigation, of which this is a preliminary note, is proceeding.

The Chairman, Mr. Crookes, gave a short verbal account of observations which he had made on the volatilisation of metals *in vacuo* under the influence of an electric discharge.

April 16th, 1891. Professor A. Crum Brown, F.R.S., President, in the Chair.

Messrs. J. C. Ayland, J. E. Marsh, G. A. Pingstone and G. H. Robertson were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. William Duncan, 10, Plough and Harrow Road, Edgbaston, Birmingham; Alfred John Gregory, The Bays, Knights Hill, West Norwood, S.E.; John Knowles, Northwich, Cheshire; Frank H. Leeds, 29, Bouverie Road, Stoke Newington, N.; Robert Andrew Scott Macfie, Rowton Hall, Chester; Frank O. Solomon, North-Eastern County School; Dr. Otto Carl Weber, Rectory Road, Crumpsall, Manchester Seward W. Williams, East Orange, New Jersey, U.S.A.

The following papers were read:—

5. "Studies on the formation of substitution derivatives." By H. Gordon, M.A.

The following notes relate to a part of a series of investigations undertaken by the author, in the laboratory of the Central Institution, with the object of throwing further light on the laws which govern substitution in the case of benzenoid compounds. It was

stated by Armstrong in 1875 (*J. Chem. Soc.*, 520), that when *parabromo*diorthonitrophenol was warmed with bromine, it underwent isomeric change into *orthobromo*orthoparadinitrophenol. Several other cases, in which perhaps a similar change takes place, were briefly discussed in the same paper. The author, at Dr. Armstrong's suggestion, has revised these observations, and, while confirming the main result, is able to correct and explain others.

The action of bromine on diorthonitrophenol.—The action of bromine on an acetic acid solution of diorthonitrophenol was found to give, at *ordinary temperatures*, the normal product, namely, *parabromo*diorthonitrophenol. On the other hand, when the mixture was heated for a short time at 100°, the product consisted of a mixture of the two isomers, *parabromo*diorthonitrophenol and *orthobromo*orthoparadinitrophenol. This mixed product by continued heating at 100° with small quantities of bromine was gradually converted into *orthobromo*orthoparadinitrophenol. *Parabromo*diorthonitrophenol is therefore completely converted by the action of heat and bromine into the isomeric orthobromorthoparadinitrophenol.

In connection with the above facts, it is of interest to note that, whereas Körner (*Gaz. Chim. Ital.*, 1874, 327—397) found that on nitrating crude bromophenol, *parabromo*dinitrophenol was obtained, Hübner and Brenken (*Ber.*, **6**, 170) obtained *orthobromo*dinitrophenol. At the time, Armstrong suggested that these facts might be explained by assuming that Hübner and Brenken had carried out the nitration in such a way as to condition isomeric change. Some experiments were made with the view to ascertain whether nitric acid would bring about this change, and it was found that by heating an acetic acid solution of *parabromo*diorthonitrophenol with a few drops of nitric acid at 100° for a short time, the whole was converted into the isomeric *orthobromo*diorthonitrophenol.

At this point it was thought important to ascertain whether similar changes could be brought about in the corresponding chloro-compounds. Some difficulty was encountered in preparing the parachlorodinitrophenol from diorthonitrophenol, as it was found that chlorine had no action on the phenol dissolved in acetic acid at 100°, even in the presence of iodine. The chlorination was effected by passing chlorine into a solution of diorthonitrophenol in antimony pentachloride heated to about 105°. Only the normal product, parachlorodinitrophenol, was obtained.

Action of bromine on parachlorodiorthonitrophenol.—Various experiments were carried out under different conditions to ascertain whether any isomeric change could be effected by the action of bromine on parachlorodinitrophenol, but in every case with negative results, the normal product, parachlororthobromorthonitrophenol,

being formed in every case, and no isomer. The result appeared to be in opposition to results published by Ling (*J. Chem. Soc.*, 1887, 789), who stated that the action of bromine at 100° on parachlor-orthonitrophenol is to form parabromorthochlororthonitrophenol. Ling, however, on repeating his experiments (*J. Chem. Soc.*, 1889, 588), found that his former statement was incorrect, and that no isomeric change had taken place. The author considers that the probable explanation of the isomeric change observed in the case of bromodinitrophenol is that the bromine first *combines* with the nitro-compound, and that, at the moment of breaking up, the bromine and NO_2 change places; in the case of the chlorine compound, a similar change does not take place, probably because the chlorine is more firmly held than bromine.

Action of sulphuric acid on orthoparadichlorophenolorthosulphonic acid.—In the paper to which reference has already been made, Armstrong indicates that possibly, by the combined action of heat and sulphuric acid, orthoparadichlorophenolsulphonic acid could be converted into the isomeric diorthochloroparaphenolsulphonic acid. As this would be a very remarkable change, the experiments were repeated under a great variety of conditions of temperature, &c., but in no case was such a change found to take place. Armstrong was no doubt misled by the presence of some diorthochlorophenol in his orthoparadichlorophenol, prepared by the action of chlorine on phenol, which gives rise to both dichlorophenols. It appeared possible that, although no isomeric change took place in the case of dichlorophenol, yet it might occur in the case of the corresponding dibromophenol. The results tended to show that this was not the case; but as several secondary reactions set in, such as the formation of tribromophenol, &c., this reaction was not further investigated.

The chlorination and bromination of phenol.—Phenol, when chlorinated in the ordinary manner, yields a mixture of para- and ortho-chlorophenol (Peterson and Bähr-Predani). As shown by Dubois in 1867, phenol may also be chlorinated by means of SO_2Cl_2, but it was not known whether the product in this case was a mixture of the two isomers; the author has therefore examined it, and finds it to be a mixture similar to that obtained by means of chlorine alone.

Further, he has investigated the action of bromine on phenol under the conditions described by Hübner and Brenken (*Ber.*, **6**, 170), and finds that the product is practically pure parabromophenol. If it be assumed that the initial action of chlorine and bromine on phenol is to form an additive compound, which then becomes resolved into hydrogen chloride or bromide and the mono-substituted phenol, it would appear that, at the moment of change, the resulting ortho-compound, in the case of bromine, at once undergoes conversion into the

para-derivative; but in the case of chlorine this change only partially takes place, owing to the chlorine being more firmly held.

The sulphonation of the nitrophenols. — Orthonitrophenol and paranitrophenol, according to experiments published by Armstrong (*J. Chem. Soc.*, 1871, 175), are both readily acted on by SO_3HCl: the former yields the well-known sulpho-acid; the product from the latter, however, is decomposed by water and is not identical with the sulpho-acid subsequently obtained by Post. It was to be supposed that the product obtained by Armstrong was the sulphate, and this the author finds to be the case. It is scarcely probable that the initial action is different in the two cases; it is more likely that the sulphate formed from the orthonitrophenol at once undergoes isomeric change, and that, owing to its greater stability, such a change does not occur in the case of paranitrophenol. The author did not succeed in obtaining any sulpho-acid by heating at 100° the sulphate from the paranitrophenol. On adding SO_3HCl (2 mols.) to paranitrophenol (1 mol.) and heating at 100°, however, a not inconsiderable amount of sulpho-acid was formed, although much of the material was carbonised.

There can be little doubt, therefore, that the paranitrophenol-sulphonic acid is formed by the sulphonation of the previously formed sulphate.

Metanitrophenol closely resembles the para-compound in being readily converted into the sulphate, but not into the sulpho-acid even by the action of heat. The author is engaged in further investigating the action of sulphonating agents on metanitrophenol.

Discussion.

Mr. A. R. Ling said that unfortunately he had made a misstatement in his work on isomeric change (Trans., 1887, 789), and he wished to thank Mr. Gordon for pointing it out; he had, however, corrected it in a subsequent communication (Trans., 1889, 588). In the latter paper, he had recorded a case of isomeric change (when orthochloroparabromophenol is nitrated), similar to that observed by Hübner and Brenken, cited by the author. Referring to the action of SO_2Cl_2 on phenol and its derivatives, Mr. Ling said that he agreed with the author that this agent yielded the same mixture of monochloro-derivatives as chlorine alone; he remembered, moreover, having once made an experiment to prepare dichlorophenol from SO_2Cl_2 and phenol, and finding that the reaction apparently stopped at the formation of the mono-derivative; this was the more remarkable as parabromophenol may readily be chlorinated by SO_2Cl_2 (*cf.* Trans., 1889, 587). His experience of the difficulty of obtaining chloro-derivatives of the nitrophenols by acting on the latter with

chlorine was the same as Mr. Gordon's, and on this account he preferred to prepare the chloronitrophenols by nitrating the chloro-derivatives. On other points, including the tendency of the bromonitro-derivatives to undergo isomeric change, and the apparent absence of this property in the case of the chloronitro-derivatives, their results were in complete accord.

6. "Compounds of dextrose with the oxides of nickel, chromium and iron." By Alfred C. Chapman.

The author describes compounds of dextrose with the oxides of nickel, chromium and iron respectively. The nickel compound was prepared by adding a solution of nickel hydrate in strong aqueous ammonia to a concentrated solution of dextrose in 90 per cent. alcohol. It is a green, amorphous substance, insoluble in water and alcohol, of the formula $C_6H_{12}O_6 \cdot 2NiO \cdot 3H_2O$.

To prepare the chromium compound, an excess of dextrose is dissolved in an aqueous solution of chromic chloride, and this solution is poured into an excess of cold strong ammonia. The precipitated hydrate partly redissolves on standing, and the purple solution so obtained gives, on pouring it into 90 per cent. alcohol, a lilac-coloured precipitate of the chromium dextrosate. The dry compound is a slate-coloured, amorphous substance, insoluble in water and alcohol. Its composition appears to be represented by the formula $C_6H_{12}O_6 \cdot Cr_2O_3 \cdot 4H_2O$. The compound of dextrose with ferric oxide is prepared by adding a slight excess of ammonia to a solution of ferric chloride in which an excess of dextrose has been dissolved. The red precipitate which at first forms soon redissolves on standing, giving a deep red solution. If this liquid be poured into 90 per cent. alcohol, a red, flocculent precipitate of the dextrosate of iron at once forms. The moist compound dissolves easily in water, giving a red solution which is decomposed on boiling, but is not decomposed by ammonia, potassic ferrocyanide or potassic thiocyanate. The dry compound is an orange-red, amorphous substance, insoluble in water and alcohol. It has the formula $2C_6H_{12}O_6 \cdot 3Fe_2O_3 \cdot 3H_2O$.

Discussion.

Remarks were made by several speakers with reference to the possible influence on the composition of such substances as described by the author of variations in the proportions of the interacting compounds, their stability in aqueous solution and their behaviour towards polarised light. Dr. Teed, referring to the circumstance that the ordinary iron reactions were not manifest in the case of the compound of iron oxide with glucose until after the addition of chlor-

hydric acid, pointed out that the thiocyanate coloration ordinarily regarded as characteristic of ferric salts was also only developed in presence of certain acids, especially chlorhydric acid. The President, referring to the tendency of chromium to form basic salts, pointed out that the formula of the chromium compound would be analogous to those of the zinc and nickel compounds if it were written $C_6H_{12}O_6 \cdot 2(CrO \cdot HO) \cdot 3H_2O$; the iron compound, however, did not appear to have an analogous composition.

The author, in reply, after describing the behaviour of the compounds when boiled with water, said that he had not yet completed their examination.

7. "A rapid method of estimating nitrates in potable waters." By G. Harrow, Ph.D.

The method depends on the reduction of nitric to nitrous acid by means of zinc-dust and chlorhydric acid, in a very dilute solution, in presence of α-naphthylamine and sulphuric acid, the estimation being made by comparing the depth of the pink azo-coloration developed in the solution with that arising on similar treatment of standard nitrate solutions. A beaker containing 50 c.c. of the water is placed on a sheet of white paper side by side with other beakers holding 50 c.c. of standard solutions containing 1·0, 0·1 and 0·01 of nitrogen as nitrate per 100.000, and to each is added 10 c.c. of a test solution, prepared by dissolving 1 gram of α-naphthylamine, 1 gram of sulphanilic acid and 25 c.c. of chlorhydric acid in abont 200 c.c. water, boiling with a small quantity of animal charcoal, filtering and making up to 500 c.c. A very small quantity of zinc-dust—7 to 8 milligrams—is added to each beaker. If nitrate be present in the water, a more or less intense pink colour is developed, which may be compared, at the end of 15 minutes, with that arising in the standard solutions. By diluting the water until the tint produced is judged to be of the same intensity as that of one of the standards—preferably the most dilute—a first approximation is arrived at; and the water, having been diluted to the extent indicated by the results, a fresh experiment is made with this diluted water. When nitrites are present, the amount is estimated in a similar manner prior to the addition of zinc-dust, and due allowance is subsequently made. The author quotes a considerable number of comparisons with the Crum method, which show that very satisfactory results are obtainable.

Discussion.

Mr. Warington said that he looked doubtfully on the method proposed, as nitrous acid was not the only product of the action of zinc.

The result would be accurate only if the conditions were precisely the same in the solutions compared. The author was right in making a final experiment in which the solutions to be compared were of the same strength. Quantitative analysis by means of colour-depths is perfectly safe only when, as in the old Nesslerising method, the final comparison is between solutions of equal strength. In not a few cases the depth of tint produced is not uniformly proportional to the quantity of substances present, very dilute solutions generally giving a weaker tint in proportion to their strength than strong solutions; this is, for instance, the case in the well-known interaction of metaphenylenediamine and nitrous acid. The speaker also questioned whether the method was more rapid than the indigo method.

Professor P. F. Frankland suggested that probably in presence of the naphthylamine, which would tend to destroy the nitrous acid as it was formed, the reduction of the nitrate would be confined to the production of nitrous acid.

8. "The 'gravivolumeter,' an instrument by means of which the observed volume of a single gas gives directly the weight of the gas: a preliminary note." By Francis R. Japp, F.R.S.

An apparatus for effecting this object has been described by Lunge (*Ber.*, **23**, 448; see also *Ber.*, **24**, 735); but his method labours under the disadvantage of requiring for each gas a separate apparatus with a special graduation. Thus Lunge's apparatus for measuring nitrogen is a "gas-volumeter," with divisions of 0·798 c.c. (further subdivided into tenths), each of which divisions will contain a milligram of nitrogen under standard conditions. The reduction to standard state is effected mechanically by means of the "regulator" attached to his gas-volumeter.

The author desires to point out how a gas-apparatus may be constructed, by means of which, with an ordinary graduation in cubic centimetres, any required single gas may, without observation of temperature or pressure, and without calculation, be measured under such conditions that each cubic centimetre represents a milligram of the gas. The form of the apparatus is, with slight modifications, that of Lunge's gas-volumeter (*Ber.*, **23**, 440); the method of employing the regulator is, however, different.

The apparatus consists of two gas burettes of, say, 50 c.c. capacity each. One of these is the gas measuring tube; the other performs the function of the "regulator" in Lunge's gas-volumeter, and may be termed the "regulator tube." Both are connected, as in Lunge's gas volumeter, by means of stout flexible tubing and a T-piece, with the *same* movable reservoir of mercury. Both are moistened intern-

ally with a drop of water, in order that the gases they contain may be saturated with aqueous vapour.

The 25 c.c. division of the regulator tube is taken as the starting point in calculating what the author terms the "gravivolumetric values" of the different gases to be measured. Thus in the case of nitrogen he calculates to what volume 25 c.c. of "standard-dry" nitrogen must be brought in order that 1 c.c. would correspond with 1 milligram of the gas: that is to say, 25 c.c. of standard-dry nitrogen $0{\cdot}001256 \times 25 = 0{\cdot}0314$ gram; and, therefore, these 31·4 milligrams of nitrogen must be brought to the volume of 31·4 c.c. The division 31·4 on the *regulator* tube is marked N_2. Corresponding points are in like manner determined for the various other gases which it is desired to measure, and these points are similarly marked O_2, CO_2, &c., as the case may be, on the regulator tube. Finally, the thermometer and barometer are read (a process which is only necessary once for all in setting the regulator); the volume which 25 c.c. of standard-dry air would occupy if measured moist at the observed temperature and pressure is calculated; and this calculated volume of air is admitted into the regulator tube and the tap closed. The instrument is now ready for use.

Suppose it is desired to ascertain the weight of a quantity of nitrogen contained in the measuring tube. The mercury reservoir is lowered until the mercury in the regulator tube stands at the nitrogen mark, 31·4, at the same time adjusting the regulator tube itself, by raising or lowering it bodily, so that the mercury level in the measuring tube and the regulator tube may be the same. *Under these circumstances each cubic centimetre of gas in the measuring tube represents a milligram of nitrogen.* For since in the regulator tube 25 c.c. of standard-dry air have been made to occupy the volume of 31·4 c.c., and as the gases in the two tubes are under the same conditions as regards temperature, pressure and saturation with aqueous vapour, therefore, in the measuring tube, every 25 c.c. of standard-dry nitrogen has also been made to occupy the volume of 31·4 c.c. But 25 c.c. of standard-dry nitrogen weigh, as we have seen, 31·4 milligrams; so that the problem is solved, and the cubic centimetres and tenths of cubic centimetres give directly the weight of the gas in milligrams and tenths of milligrams.

The various other single (*i.e.*, unmixed) gases may be weighed in like manner by bringing the mercury in the regulator tube to the "gravivolumetric mark" of the gas in question, and adjusting the levels as before. An exception would be made in the case of hydrogen, which would be brought to such a volume that the cubic centimetre would contain a *tenth* of a milligram.

Lastly, if the mercury in the regulator tube be brought to the

mark 25, a gas or mixture of gases in the measuring tube will have the volume which it would occupy in the standard-dry state. In this form the instrument is merely a gas-volumeter, as described by Lunge, and may be employed for ordinary gas analyses.

The "gravivolumeter" is thus designed to fulfil a variety of purposes for which Lunge employs a number of different gas-volumeters. Whether it will fulfil these purposes equally well remains to be seen. The theoretical principle is unimpeachable; but there are doubtless practical difficulties to be overcome before the "gravivolumeter" can rank as a working laboratory appliance. Very likely the foregoing (merely provisional) dimensions of the regulator would have to be increased in order to give sufficient accuracy of adjustment. The author proposes to have the instrument constructed in various forms, so as to ascertain the most suitable. He anticipates that it will, at all events, give results sufficiently accurate for technical purposes. Meanwhile he desires, by this preliminary note, to place on record this principle of gas analysis, which he believes to be new—the principle of measuring the various single gases at such a volume that each cubic centimetre contains a milligram of the gas.

Mr. DE MOSENTHAL exhibited one of Lipmann's "coloured" photographic negatives.

9. "The action of acetic acid on phenylthiocarbimide." By J. C. Cain and J. B. Cohen, Ph.D., Owens College, Manchester.

The authors have repeated the experiments of Hofmann, and show that the product of the action of pure glacial acetic acid on phenylthiocarbimide is not diacetanilide as stated by Hofmann; but that two compounds are formed, viz.: diphenylurea and acetanilide. The proportion of these products depends upon the temperature at which the mixture is heated. At a lower temperature, diphenylurea is mainly formed, and at a higher temperature, acetanilide.

The action, which appears to take place in two stages, may be expressed by the following equations:—

1. $2C_6H_5NCS + 6C_2H_4O_2 = (C_6H_5NH)_2CO + 3(C_2H_3O)_2O + 2H_2S + CO_2.$

2. $(C_6H_5NH)_2CO + 2C_2H_4O_2 = 2C_6H_5NH_2 + (C_2H_3O)_2O + CO_2.$

These interactions are independent of the presence of water.

10. "The action of aluminium chloride on benzenoid acid chlorides." By R. E. Hughes, Jesus College, Oxford.

At Mr. Marsh's suggestion, the author has examined the action of

aluminium chloride on cinnamic and hydrocinnamic chlorides in the expectation that pentamethylene derivatives might result from the occurrence of an internal condensation analogous to the external condensation which attends the formation of acetophenone from acetyl chloride and benzene, thus—

$$CH_3{\cdot}COCl + C_6H_6 = CH_3{\cdot}CO{\cdot}C_6H_5 + HCl.$$

$$C_6H_5{\cdot}CH{\cdot}CH{\cdot}COCl = C_6H_4{<}\begin{matrix}CO\\CH\end{matrix}{>}CH + HCl.$$

The experiments have, however, afforded negative results. The chloride was either dissolved in or mixed with (in the case of hydrocinnamic chloride) light petroleum, and aluminium chloride was then added; action set in at 80—90° in the case of cinnamic, and at about 50° and more briskly in the case of hydrocinnamic, chloride. The chief product in either case was an ill-characterised substance, the nature of which remains to be determined. Both chlorides afforded a small amount of the aluminium salt of the corresponding acid in the form of a microcrystalline powder, insoluble in alcohol, benzene, ether and petroleum, slightly soluble in a warm solution of sodium carbonate.

The author incidentally describes the following hydrocinnamic derivatives.

Hydrocinnamic chloride, $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}COCl$, boils at 117—119°, under 13 mm. pressure; the author specially points out that the properties of this chloride are strikingly similar to those of benzoic chloride and characteristically different from those of cinnamic chloride, which, unlike most acid chlorides, is a remarkably inert substance, being only very slowly decomposed by water or caustic alkalis.

Hydrocinnamide crystallises from hot alcohol, in which it is readily soluble, in stellate groups of needles melting at 82°; it is readily soluble in hot water.

Hydrocinnamanilide crystallises from hot alcohol in faintly yellow plates melting at 92°.

It is noted that benzoic and cinnamic acids may be readily separated by treating the the mixture with phosphorus pentachloride and distilling the product under reduced pressure; the portion passing over below 95° under 10 mm. pressure contains the benzoic chloride.

ADDITIONS TO THE LIBRARY.

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Lehrbuch der Mikrophotographie, von R. Neuhaus. Braunschweig 1890.

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Lehrbuch der physiologischen Chemie, von O. Hammarsten. Aus der zweiten schwedische Auflage übersetzt vom Verfasser. Wiesbaden 1890.

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Das Totalreflectometer und das Refractometer fur Chemiker, von C. Pulfrich. Leipzig 1890.

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Outlines of General Chemistry, by W. Ostwald. Translated by J. Walker. London 1890.

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At the next meeting, on May 7th, there will be a *Ballot* for the election of Fellows.

The following papers will be read:—

"The action of alkalis on the nitro-compounds of the paraffin series." By Professor Dunstan and Mr. T. S. Dymond.

"The addition of the elements of alcohol to the ethereal salts of unsaturated acids." By Professor Purdie and W. Marshall.

"Note on the azo-derivatives of β-naphthylamine." By Professor Meldola, F.R.S., and Frank Hughes.

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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 97. Session 1891-92.

May 7th, 1891. Dr. J. H. Gladstone, F.R.S., Vice-President, in the Chair.

Certificates were read for the first time in favour of Messrs. Edward Brown, 32, Courlandsky Street, St. Petersberg; Ernest A. Congdon, Lehigh University, St. Bethlehem, U.S.; W. Porter Draper 1, Ceal Villas, Ceal Road, Enfield; Thomas Mitchell, c/o E. Mitchell, Crossmount, Bridgend, N.B.; H. J. Marston Mousley, Kingsbury, Portland Road, Edgbaston; Edward Rhodes, Holybank, Frodsham, Cheshire; John Taylor, 15, Lucius Street, Torquay.

The following were elected Fellows of the Society:—Messrs. Edward Arthur Barnes, William Bate, Claude Hooper Bater, Albert Edward Bell, Rhys Pendrilt Charles, Walter Johnson Cooper, Frederick Arthur Evans, Gilbert John Fowler, Joseph Fitze, John Alfred Foster, Berington H. Gibbins, William L. Hiepe, Ph.D., William Beaumont Hart, Walter Herbert Joseland, F. Stanley Kipping, D.Sc., Alexander Lauder, Rev. Edgar Norman Langham, James Leicester, George R. Morrison, William Macdonald, Charles Ainsworth Mitchell, Frederick Johnson Merrils, Lewis Ough, Percy Morris Randall, James Ashburner Storey, Albert Searl, James Fowler Tocher, Cecil George Freer Thonger, M.R.A.C., John Wild.

The Chairman announced that since the last meeting of the Society took place a congratulatory address, of which the following is the text, had been forwarded to Professor Stas:—

We, the President, Officers and Council, on behalf of the Chemical

Society, most heartily congratulate you, Professor Jean Servais Stas, on the completion of your fiftieth year of membership of the Royal Belgian Academy of Sciences, Literature and Arts.

Among the names of the distinguished investigators who have raised chemistry to the dignity of an Exact Science, none either merits or receives a more honoured position than that of Stas. Your researches are universally recognised among men of science as of fundamental importance. By your incomparable determinations of the atomic weights of a large number of the more important elements you have not only placed in our hands numerical data of the utmost value, but your researches are models which must ever serve to show how such determinations should be effected and the innumerable precautions which must be taken. Concerning these precautions comparatively few, even among chemists, fully realise the extent to which they have been shown by you to be necessary: those who have been engaged in similar investigations can only entertain an admiration almost reverential in character for the man who could plan and successfully carry out a prolonged series of such refined, tedious and delicate operations. A most important result of your inquiries has been the refutation, in its original form at least, of the famous hypothesis of Prout: your marvellously accurate determinations showing that it is no longer possible to believe that the atomic weights of the elements are expressible as a series of multiple whole numbers. With strict logical propriety you have refrained from pronouncing any opinion in explanation of the discrepancy; the data which you have established, however, will surely serve in the future as the groundwork of further discussion of the problem of the mass relationship of the elements. The methods which you have devised for the preparation of pure substances have, in many cases, in themselves been important contributions to chemical science; and the service which you have rendered by teaching the chemist how to prepare pure reagents is of the utmost value. Hence your *Recherches sur les Rapports réciproques des Poids atomiques* must be handed down to future generations as one of the most valuable classics of the Exact Sciences. Apart from the intrinsic value of your work, you have through it exercised a beneficent influence on your colleagues throughout the world, the importance of which cannot be overestimated; and in the eyes of chemists generally, you are ever regarded as an honour to Science, to your country and to the distinguished Academy of which you have now been an ornament for half a century.

The following papers were read:—

11. "The action of alkalis on the nitro-compounds of the paraffin series." By Wyndham R. Dunstan and T. S. Dymond.

The authors have further investigated the conditions and products of the interaction of alkalis and nitroethane, of which they have already given a preliminary account to the Society (Proc., 1888, 117).

Nitroethane attacks alkali carbonates in the cold with formation of carbon dioxide and the alkali derivative of nitroethane which is also obtained when alkali hydroxide is employed. Ammonia combines with nitroethane in the cold to form a crystalline compound analogous to the potassium and sodium derivatives. The action of alkalis does not appear to proceed further at atmospheric temperatures, but on warming, alkali nitrite, acetonitrile and a new compound, boiling at 171° and freezing to a crystalline solid at 3·5°, are produced. The new compound is a feeble base, which forms unstable salts decomposed by water: the *mercurichloride* has the formula $C_6H_9NO,HgCl_2$, and the *aurichloride* the formula $C_6H_9NO,AuCl_3$. It is remarkable for its great stability, being almost unaffected by heating in closed tubes with strong acids and alkalis. Permanganate oxidises it to acetic acid, and nitric acid to acetic and oxalic acids. It is hard to attack with the usual reducing agents, but is slowly decomposed with formation of ammonia, acetic acid and secondary butyl alcohol. By acting with sodium on a well cooled moist ethereal solution, a *dihydride* is formed ($C_6H_{11}NO$): this is a crystalline compound (m. p. 110°, corr.), which is resolved by heating with water into ammonium acetate and ethyl methyl ketone.

The interactions of the compound prove that it is neither a pyridine nor pyrrol derivative nor a keto-cyanide. Most of its properties are consistent with the view that it is either a trimethyloxazole or a trimethylisoxazole.

Trimethyloxazole was produced by the interaction of acetamide and bromethyl methyl ketone.

$$\underset{\text{(Bromethyl methyl ketone).}}{CH_3\cdot CO\cdot C(CH_3)HBr} + CH_3\cdot CO\cdot NH_2 = \begin{array}{c} CH_3\cdot C{=}C\cdot CH_3 \\ \quad\ N\quad O \\ \quad\ \diagdown\!\diagup \\ \quad\ C\cdot CH_3 \end{array} + H_2O + HBr.$$

This oxazole was found to have some properties in common with the substance under investigation, but in other respects was entirely different, especially in its physical characters.

Trimethylisoxazole was prepared by acting on the β-diketone, methyl acetyl acetone with hydroxylamine. It may be supposed that the monohydroxime is first formed, and that this then loses water.

$$\begin{array}{l} CH_3C{:}NOH \\ CH_3CH \\ CH_3CO \end{array} = H_2O + \begin{array}{l} CH_3C{:}NO \\ CH_3C \\ CH_3C \end{array}\!\!\diagup$$

The trimethylisoxazole thus produced is in every respect identical with the compound obtained from nitroethane.

Nitropropane when acted on by alkalis yields triethylisoxazole, $C_2H_5{\cdot}C{=}C{\cdot}C_2H_5$ / $C_2H_5{\cdot}C\quad O$ \ / N, propionitrile and alkali nitrite, but interaction occurs with greater difficulty than in the case of nitroethane.

Nitromethane is very readily attached by alkalis with formation of hydrogen cyanide, alkali nitrite and much resin. The parent isoxazole, $HC{=}CH$ / $HC\quad O$ \ / N, could not be isolated, but the interaction is still being investigated.

Secondary nitropropane is attacked with difficulty by alkalis. Alkali nitrite is produced, but no isoxazole.

12. "Some new addition compounds of 'thiocarbamide' which afford evidence of its constitution." By J. Emerson Reynolds, M.D., F.R.S.

In the course of the author's work on silicon compounds, a thiocarbamide derivative containing silicon tetrabromide was obtained which broke up on treatment with ethyl alcohol, affording among other products the fine crystalline substance $(H_4N_2CS)_4H_4NBr$. The same compound was subsequently obtained by direct union of its components as was described in a former paper (Trans., **53**, 857). This substance proved to be the first of a series, and the present paper gives an account of their detailed examination of all the members prepared. The following is a summary of the results of the investigation :—

1. Thiocarbamide combines with ammonium bromide, iodide and chloride at the temperature of boiling alcohol, forming characteristic compounds of the type $(H_4N_2CS)_4H_4NR'$. But no compounds were formed under the conditions specified which contained fewer than four molecular proportions of amide to one of ammonium salt.

2. The following mono- and di-substituted thiocarbamides failed to afford any compounds with ammonium bromide at the temperature of boiling alcohol, viz. :—methyl-, ethyl-, allyl-, phenyl-, diphenyl- and acetylphenyl-thiocarbamides.

3. Thiocarbamide combines with tetrethylammonium bromide and iodide forming well-defined crystalline compounds of the type $(H_4N_2CS)_2Et_4NR'$. No well-defined substance could be isolated under any of the experimental conditions containing more than 2 mols. of the amide and 1 of the tetrethylammonium salt.

4. Thiocarbamide combines with diethylammonium bromide forming a well-crystallised compound, $(H_4N_2CS)_3Et_2H_2NBr$. If a tetra-compound be formed in solution, it is certainly broken up on slow crystallisation.

5. Thiocarbamide also unites with triethylammonium bromide, and in presence of excess of amide a somewhat felted mass is obtained, which on recrystallisation affords two distinct forms of crystals, viz. :—

$$(H_4N_2CS)_3Et_3HNBr \text{ and } (H_4N_2CS)_2Et_3HNBr.$$

6. With methylammonium bromide, thiocarbamide afforded the compound $(H_4N_2CS)_4MeH_3NBr$, which resembles the corresponding ammoninm bromide compound in appearance, but melts at a temperature 34° lower. On the other hand, with *ethyl*ammonium bromide, no combination whatever could be effected, and when the amide and salt in the molecular proportions 4 : 1 were heated in a pressure tube to 135° with alcohol, ethyl oxide and *tetrathiocarbamidammonium bromide* were the products.

The author shows that the foregoing facts are not in agreement with the view that thiocarbamide is $CS(NH_2)_2$, bnt are altogether in favour of the unsymmetrical structure $HN{:}C(SH)NH_2$.

It is pointed out that an interesting practical application of the compound $(H_4N_2CS)_4H_4NBr$ has recently been made by Colonel Waterhouse to the production of *direct positive* photographs. So effective is the agent in secnring the reversal of the photographic image, that the presence of only $\frac{1}{100}$th of a grain per ounce of "eikonogen" developer causes the negative image that first appears to change into a rich coloured positive.

Discussion.

Referring to the reversed photographs exhibited by Professor Reynolds, Mr. Groves drew attention to the curious fact that the silver deposit which, in the early stage of development, apparently behaved like that forming an ordinary negative image, in the later stage became soluble.

13. "The action of acetic anhydride on substituted thiocarbamides; and an improved method for preparing aromatic mustard

oils." By Emil A. Werner, Assistant Lecturer in Chemistry, Trinity College, University of Dublin.

The present investigation originated from an experiment carried out with the object of obtaining an acetylated diphenylthiocarbamide by the action of acetic anhydride on sulphocarbanilid. The action of the anhydride on diphenyl-, ortho-, meta- and para-ditolyl-, meta-dixylyl, dibenzyl- and diethyl-thiocarbamides has been studied. In the case of the benzenoid derivatives, the results are summed up in the following statements :—

1. No acetylated derivatives of the thiocarbamides were produced.

2. The mere dissolution of the thiocarbamide in acetic anhydride is accompanied by simultaneous decomposition into "anilid" and mustard oil in accordance with the equation

$$CS(NHR)_2 + (CH_3CO)_2O = CH_3CONHR + R{\cdot}NCS + CH_3COOH.$$

3. *Five minutes* heating at the boiling point of acetic anhydride gives an almost theoretical yield of mustard oil.

4. An extension of the time of heating induces a secondary interaction between the mustard oil and acetic acid, whereby the yield of the former is rapidly diminished, viz.,

$$R{\cdot}NCS + CH_3COOH = CH_3CONHR + COS.$$

Curves are given in the original paper, showing the influence of time on the rate of fall in the yield of mustard oil.

In the case of the paraffinoid thiocarbamides the results are different.

1. A well-defined acetylated thiocarbamide is first produced.

2. Further heating gives rise to the formation of mustard oil, but the yield of the latter is never high, on account of the secondary interaction proceeding simultaneously with the generation of the mustard oil.

3. Prolonged heating gives a substituted amide as final product.

Acetyldibenzylthiocarbamide, $CS(NH{\cdot}CH_2Ph)(NAc{\cdot}CH_2Ph)$, prepared from dibenzylthiocarbamide, crystallises from alcohol in prisms; m. p. 93° C. The alcoholic solution is not desulphurised by boiling with alkaline lead tartrate. With $AgNO_3{\cdot}2NH_3$ it gives a white precipitate. It decomposes partly on distillation, yielding between 175—180° an oil rich in sulphur, and between 180—190° the distillate solidifies to a substance which after purification forms colourless crystals melting at 60—61° and free from sulphur.

Acetylbenzylthiocarbamide, $CS(NH{\cdot}CH_2Ph)(NH{\cdot}CO{\cdot}CH_3)$, was incidentally prepared from acetic anhydride and monobenzylthiocarbamide. It crystallises from alcohol in thin, rhombic prisms; m. p. 129—130°. The alcoholic solution, unlike that of the previous compound, desulphurises alkaline lead solution on boiling, and with

$AgNO_3{\cdot}2NH_3$ gives a white precipitate which darkens on standing and is immediately blackened on boiling. On distillation, the urea decomposes partly into CH_3CONCS and benzylamine and partly into benzylthiocarbimide and acetamide.

14. "The decomposition of silver chloride by light." By Arthur Richardson, University College, Bristol.

The author describes experiments which have been made with a view to determine whether silver chloride which has been darkened by exposure to light under water contains oxygen. The nature of the change which occurs during decomposition of the chloride was also studied with reference to the part played by water.

Pure silver chloride was prepared by addition of dilute chlorhydric acid to a solution of pure silver nitrate, the precipitate being washed by decantation till free from acid. The following facts were observed during exposure:—

(1.) Oxygen was evolved, a part of which was present as ozone.

(2.) When small quantities of water were present, chlorine and hydrogen chloride were found in solution.

(3.) When a large volume of water was taken, hydrogen chloride, but no chlorine, was detected.

The influence of hydrogen chloride in retarding the decomposition of silver chloride is considered, and is explained from experimental results given, which show that even minute quantities of hydrogen chloride exercise a marked influence on the stability of chlorine water when exposed to light, the rate of decomposition of the silver chloride being dependent on the readiness with which the chlorine in solution and water interact to form hydrogen chloride. Thus, when silver chloride was exposed to light in a solution of hydrogen chloride containing 0·9 part per 100 of solution, the total chlorine liberated was 0·201 gram, of which 13·7 per cent. represented free chlorine, whilst for the same weight of silver salt in pure water the total chlorine found was 0·276 gram, of which 0·9 per cent was present as free chlorine.

In the examination of the darkened product for oxygen, a portion of the substance was taken which had lost 8 per cent. of its total chlorine during exposure. After it had been dried at 110° C. till it ceased to lose weight, it was heated in a current of pure hydrogen, the gaseous products of the reduction being passed through a weighed phosphorus pentoxide tube. Before using this substance as an absorbent of moisture, it was ascertained that hydrogen chloride was not absorbed by it after contact for a few hours only, as the weight of the tubes remained unaltered in contact with the dry

gas. The hydrogen was prepared by the action of steam on sodium, numerous precautions, which are described in full in the paper, being taken to preclude errors.

The results show that the gain in weight of the drying tubes after the decomposition of the silver compound, which lasted from 7—8 hours, is so small as to preclude the possibility of the presence of an oxygen compound in the darkened product. The darkening of the carefully dried chloride was also observed to take place when exposed to light in a tube containing dry carbon tetrachloride from which all air had been removed by boiling. From these facts the author concludes that the darkened silver compound is of the nature of a subchloride rather than an oxychloride.

15. "The addition of the elements of alcohol to the ethereal salts of unsaturated acids." By T. Purdie, Ph.D., B.Sc., and W. Marshall, B.Sc.

In this paper the authors record the results of further experiments on the addition of the elements of alcohol to ethereal salts of fumaric and maleic acids by the agency of small quantities of sodium alkylate; they also describe a series of similar experiments with other ethereal salts, the object of which was to ascertain if the ethereal salts of unsaturated acids in general are capable of undergoing the same additive change.

By the action of small quantities of sodium methylate in the cold on a mixture of methyl alcohol and methylic fumarate, the latter is converted, almost quantitatively, into methylic methoxysuccinate, which crystallises in very large and perfectly developed crystals melting at 28°. Methylic methoxysuccinate from methylic maleate is identical with that obtained from methylic fumarate. Methoxysuccinamide, from the action of alcoholic ammonia on the ethereal salts, melts at 175°.

From the product of the action of alcoholic sodium methylate on methyl fumarate aided by heat, an amorphous substance was obtained, the composition of which agreed with that of a compound having the formula $C_{11}H_{12}O_7$, formed by the abstraction of 3 mols. of methyl alcohol from 2 mols. of methylic methoxysuccinate.

By the action of small quantities of sodium methylate on a mixture of methylic acrylate and methyl alcohol, methylic methoxypropionate was obtained.

Methylic and ethylic crotonate gave, in a similar manner, methylic methoxybutyrate and ethylic ethoxybutyrate respectively. The metallic salts of these acids are mostly gums or resins, but the acid amines are crystalline; the methoxybutyramide melts at 69°, and

the corresponding ethoxy-derivative at 75°. The authors think that in the interaction under consideration, the alkoxy-group attaches itself to the β-carbon atom, but the evidence on this point is not conclusive.

Ethylic methacrylate seems also to be capable of combining with the elements of alcohol, but pure products were not obtained.

Ethylic angelate, ethylic allylacetate, methylic and ethylic cinnamate and ethylic *o*-(β-)ethylcumarate were found incapable of the additive change under investigation. Similar experiments were made with ethylic phenylpropiolate, but no additive product was obtained.

The ethereal salts of unsaturated acids differ greatly in respect of their capability of combining with the elements of alcohol under the agency of sodium alkylate. This capability is, no doubt, affected by the position of the doubly-linked carbon atoms and by the nature of the atomic groups with which they are united. It is, however, impossible at present to draw any general conclusion regarding the influence of these factors.

16. "Notes on the azo-derivatives of β-naphthylamine." By Raphael Meldola, F.R.S., and Frank Hughes.

The authors have completed the series of azo-derivatives obtainable from the nitranilines and β-naphthylamine by preparing orthonitrobenzeneazo-β-naphthylamine. This compound crystallises in bronzy scales; m. p. 198°. When acted on by sodium nitrite in a warm glacial acetic acid solution, it gives orthonitrobenzeneazo-β-naphthol,

$$C_{10}H_6\begin{matrix}N_2\cdot C_6H_4\cdot NO_2(o)\\ N_2\cdot OH(\beta)\end{matrix} = C_{10}H_6\begin{matrix}N_2\cdot C_6H_4\cdot NO_2(o)\\ OH(\beta)\end{matrix} + N_2.$$

The latter forms bright red needles; m. p. 209—210°. When the interaction is effected in a cold acetic acid solution, the naphthyl acetate is formed,

$$C_{10}H_6\begin{matrix}N_2\cdot C_6H_4NO_2(o)\\ N_2\cdot OH(\beta)\end{matrix} + HO\cdot C_2H_3O = C_{10}H_6\begin{matrix}N_2\cdot C_6H_4\cdot NO_2(o)\\ O\cdot C_2H_3O(\beta)\end{matrix} + N_2 + H_2O.$$

The latter is a deep red oil, from which the acetyl group is easily removed by alkalis. Acetyl derivatives of the ortho-, meta- and para-nitroazo-derivatives of β-naphthylamine have also been prepared,

$C_{10}H_6<^{N_2\cdot C_6H_4\cdot NO_2(o)}_{NH\cdot C_2H_3O(\beta)}$ .... Dull orange needles; m. p. 154°.

$C_{10}H_6<^{N_2\cdot C_6H_4\cdot NO_2(m)}_{NH\cdot C_2H_3O(\beta)}$ .. Bright orange needles; m. p. 192°.

$C_{10}H_6<^{N_2\cdot C_6H_4\cdot NO_2(p)}_{NH\cdot C_2H_3O(\beta)}$ .. Dull red needles; m. p. 227—228°.

The pseudazimides from the para- and meta-nitro-compounds have been prepared by Zincke's method of oxidation with chromic acid in glacial acetic acid solution. The first of these crystallises in flat, colourless needles, m. p. 236°, and the second in whitish needles of m. p. 224°. The ortho-compound gives but a very small quantity of pseudazimide on oxidation. The formula of these compounds is $C_{10}H_6<^{N}_{N}>N\cdot C_6H_4\cdot NO_2$ (*p* or *m*). The action of aldehydes on these β-naphthylamine azo-derivatives gives rise to the formation of triazines, which are being investigated. Fuming nitric acid in the cold converts the azo-compounds into orange, amorphous products which are apparently definite, but difficult to purify and explosive.

17. "The estimation of nitrates." By G. McGowan, Ph.D.

The author describes a method of estimating nitrates based on the interaction $HNO_3 + 3HCl = NOCl + Cl_2 + 2H_2O$. The nitrate is warmed together with an excess of concentrated chlorhydric acid in an apparatus from which air has been expel ed by CO_2, and the gaseous products are led into a solution of potassium iodide; an amount of iodine is liberated equivalent to the whole of the chlorine carried forward, nitric oxide escaping, *i.e.*, $HNO_3 = 3Cl$.

18. "New benzylic derivatives of thiocarbamide." By Augustus E. Dixon, M.D.

A re-examination of "monobenzylthiocarbamide" has shown that the substance hitherto bearing this name is really benzylamine thiocyanate; the latter can be converted into the isomeric thiocarbamide by heating for a short time at 150—160°. The melting point recorded for symmetrical dibenzylthiocarbamide also requires correction; it lies between 146° and 147°, and not at 114°, as stated.

The following compounds are described:—

Benzylthiocarbamide, $Ph\cdot CH_2\cdot NH\cdot CS\cdot NH_2$, small, white prisms; m. p. 161—162°.

Benzylorthotolylthiocarbamide, $Ph\cdot CH_2\cdot NH_2\cdot CS\cdot NHoTo$, white, rhombic prisms; m. p. 138—139°.

Benzylmetatolylthiocarbamide, $Ph{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}NH\,m\mathrm{To}$, glassy-clear rhombs, m. p. 113—114°.

Benzylparatolylthiocarbamide, $Ph{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}p\mathrm{To}$, glassy, rhombic crystals; m. p. 120—121°.

Benzylmetaxylylthiocarbamide, $Ph{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_3Me_2$, large, colourless, monoclinic prisms; m. p. 84—85°.

Benzylalphanaphthylthiocarbamide, $Ph{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_{10}H_7$, micaceous-looking rhombs; m. p. 172—173°.

Benzylbetanaphthylthiocarbamide, rhombic plates; m. p. 165—166°.

Allylbenzylthiocarbamide, $Ph{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}All$, colourless, rhombic crystals; m. p. 93—94°. Converted by heating with HCl at 100° into—

Benzylpropylene-ψ-thiocarbamide, $\begin{matrix}CH_3{\cdot}CH-S\\ \quad\quad|\\ \quad CH_2{\cdot}N\end{matrix}\!\!>\!C{\cdot}NH{\cdot}CH_2Ph$, fine, white needles; m. p. 65—66°.

Acetylbenzylthiocarbamide, $Ph{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}NHAc$, thin, pearly plates; m. p. 128—129°.

Benzylmethylphenylthiocarbamide, $Ph{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}NMePh$, white prisms; m. p. 84—85°.

Methylphenylbenzylthiocarbamide, $MeNH{\cdot}CS{\cdot}NPh{\cdot}CH_2Ph$, shining, white prisms; m. p. 120—121°.

Benzylethylphenylthiocarbamide, $Ph{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}NEt{\cdot}Ph$, long, slender, oblique prisms; m. p. 90—91°.

Ethylbenzylphenylthiocarbamide, $Et{\cdot}NH{\cdot}CS{\cdot}NPh{\cdot}CH_2Ph$, short, thick, rectangular prisms; m. p. 90·5—91°.

Benzylphenylbenzylthiocarbamide, $Ph{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}NPh{\cdot}CH_2Ph$, white, pointed prisms; m. p. 102—103°.

Benzylpiperidylthiocarbamide, $Ph{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}NC_5H_{10}$, waxy-looking prisms; m. p. 87—88°.

19. "Interaction of phenylthiocarbimide and acetic acid." By Emil A. Werner, Trinity College, Dublin.

This interaction was originally made the subject of an experiment by Professor von Hofmann, and later on by Claus and Völtzkow; the former considered diacetanilid to be the product, while the latter simply mention acetanilid as being formed.

In neither case was the examination of the products exhaustive. The author has made a careful re-investigation of the subject, and wishes to state his results at once, as an abstract of a paper, by Messrs. Cain and Cohen, on the same interaction, appeared in the last Proceedings. The author agrees with Messrs. Cain and Cohen, that diacetanilid is not formed, but his results oblige him to differ entirely from these gentlemen with respect to the course of the change.

The influence of water on the nature of the interaction is very marked. With *pure anhydrous* acetic acid and phenylthiocarbimide, interaction takes place, *quantitatively*, at 130—140°, in accordance with the equation: $C_6H_5NCS + CH_3COOH = CH_3CONHC_6H_5 + COS$.

If the acid *contain water*, H_2S, CO_2 and diphenylurea are formed as products of a secondary change, viz.: $2C_6H_5NCS + 3H_2O = CO(NHC_6H_5)_2 + CO_2 + 2H_2S$.

At a higher temperature, 160—170°, the diphenylurea disappears, through interaction with acetic acid, thus: $CO(NHC_6H_5)_2 + 2CH_3COOH = CH_3CONHC_6H_5 + CO_2 + H_2O$, the extent to which this change takes place increases, within certain limits, with the proportion of water present in the acid.

Propionic acid and phenylthiocarbimide interact in a similar manner, but with formic acid a secondary interaction takes place, which appears to be independent of the presence of water.

RESEARCH FUND.

Fellows desiring grants are requested to forward their applications to the Secretaries, in order that they may be considered at a meeting early in June.

At the next meeting, on May 21st, the following papers will be read:—

"The bromo-derivatives of β-naphthol;"

"the action of nitric acid on derivatives of phenols as indicative of the manner in which nitration is effected in the case of benzenoid compounds generally." By Henry E. Armstrong and E. C. Rossiter.

"Nitrification. Part IV." By R. Warington, F.R.S.

HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY, ST. MARTIN'S LANE.

Issued 16/6/1891.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 98. Session 1891–92.

May 21st, 1891. Professor A. Crum Brown, F.R.S., President, in the Chair.

Messrs. J. A. Foster, William MacDonald and F. H. Moore were ormally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Frederick R. Holloman, Sugar Refinery, Rawcliffe Bridge, Selby; Arthur Michael, Torwood, Bonchurch, Isle of Wight; F. M. Perkin, Heriot Watt College, Edinburgh; Edmund Charles Rossiter, 39, Brook Green Road, Hammersmith; John Shields, The Byers, Bathgate, N.B.

The President announced that Dr. William Wegg had presented to the Society, through Mr. Warington, a daguerreotype containing the portraits of Messrs. Brande, Cooper and Phillips.

The following papers were read:—

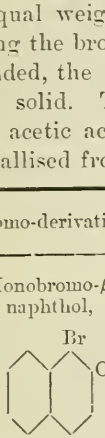
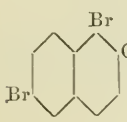
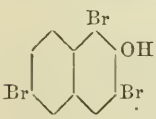
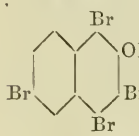
20. "Bromo-derivatives of betanaphthol." By Henry E. Armstrong and E. C. Rossiter.

The authors have completed the study of the compounds formed on brominating betanaphthol, to which they have referred in two previous notices (these Proceedings, 1889, 71; 1890, 32). They give the following directions for the preparation of tri- and tetra-bromobetanaphthol.

Tribromo-β-naphthol is prepared by adding somewhat more than three molecular proportions of bromine to betanaphthol dissolved in thrice its weight of acetic acid; the solution becomes hot, but must *not* be cooled. When all the bromine is added, the mixture is allowed to stand during one hour, and is then heated on the water-bath, at

first gently, afterwards at 100°, as long as hydrogen bromide is evolved. The white, solid product is recrystallised once or twice from acetic acid, and then treated with twice the theoretical quantity of acetic chloride. The acetate is purified by crystallisation from acetic acid and benzene. When treated with alcoholic potash, it is easily converted into tribromonaphthol.

Tetrabromo-β-naphthol is prepared by adding somewhat more than four molecular proportions of bromine to betanaphthol mixed with an equal weight of acetic acid. The solution becomes very hot on adding the bromine, but must not be cooled. When all the bromine is added, the mixture is heated on the water-bath until it becomes quite solid. The product is purified by crystallising once or twice from acetic acid. It is then converted into the *acetate*, and this is crystallised from a mixture of benzene and acetic acid.

Bromo-derivative.	Description.	Acetate.	Convertible by HNO_3 into
Monobromo-β-naphthol, 	Slender needles very soluble in acetic acid. M. p. 84°.	—	α_1-nitro-β-naphthol. M. p. 103°.
Dibromo-β-naphthol, 	Long, shining needles moderately soluble in acetic acid. Crystallised with 1 mol. prop. of acetic acid, m. p. 84°. M. p. 106°.	Elongated, lustrous plates. M. p. 125°.	$C_{10}H_5BrO_2$. M. p. 145°. $C_{10}H_4Br_2O_2$. M. p. 171°. α_1-nitrobrom-β-naphthol. M. p. 122.°
Tribromo-β-naphthol, 	Lustrous needles less soluble than the dibromo-compound. M. p. 155°.	Soft, interlacing needles. M. p. 184°.	$C_{10}H_4Br_2O_2$. M p. 150° α_1-nitrodibrom-β-naphthol. M. p. 163°.
Tetrabromo-β-naphthol, 	Very slender, silky needles sparingly soluble in acetic acid. M. p. 172°.	Short, colourless, prismatic needles. M. p. 189—190°.	$C_{10}H_3Br_3O_2$. M. p. 190°. α_1-nitrotribrom-β-naphthol darkens at 135°; melts at 136° with decomposition.

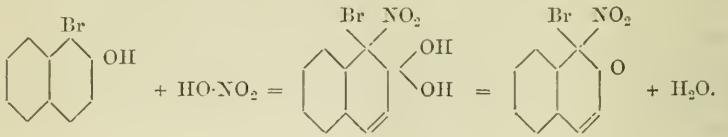
The properties of the bromobetanaphthols are summarised in the table on p. 88. The preparation of the bromobetanaphthaquinones and of the α-nitrobromonaphthols, included in the fourth column of this table, is described in the next note.

The entire product of the action of bromine in excess on betanaphthol has been carefully examined without any substance having been discovered which affords 1 : 2 : 3-bromophthalic acid on oxidation; the explanation of the discrepancy between the authors' observations and the earlier experiments of Smith and Meldola, therefore, yet remain to be discovered.

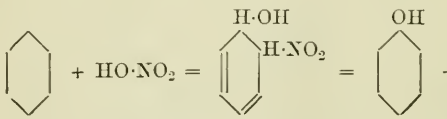
21. "The action of nitric acid on naphthol derivatives as indicative of the manner in which nitration is effected in the case of benzenoid compounds generally. The formation of nitro-keto-compounds." By Henry E. Armstrong and E. C. Rossiter.

When warmed with nitric acid, the chloro- and bromo-derivatives of betanaphthol are converted into derivatives of betanaphthaquinone, but, as the authors have pointed out in their previous notice, the formation of these products is preceded by that of an unstable intermediate compound. When these intermediate compounds are carefully heated, they are converted into bromo-derivatives of betanaphthaquinone, and in preparing these latter it is desirable to separate the intermediate compound from the excess of nitric acid, and to decompose it by carefully heating it with acetic acid, except in the case of tetrabromobetanaphthol; tribromobetanaphthaquinone is so readily formed from this compound, and is so difficultly soluble and well characterised, that small quantities of tetrabromobetanaphthol may be detected in presence of the di- and tri-bromo-derivatives by simply heating the mixture with acetic acid and nitric acid. Thus, if nitric acid be added to dibromobetanaphthol, suspended in acetic acid, a clear solution is obtained, which, after a short time, deposits a crystalline substance; if quickly separated by filtration, this product is almost colourless, but it decomposes when kept, becoming yellow. It was conceivable, judging from the manner in which it was produced, that the compound was a nitrate, formed by the simple displacement of the hydroxylic hydrogen by NO_2, and the results of analysis were in accord with this view; but such a nitrate should be reconvertible into the parent substance by treatment with alkali, whereas actually it affords, as chief product, *bromonitronaphthol*. Bromobetanaphthol, in like manner, eventually yields α_1-nitrobetanaphthol, and the tri- and tetra-bromo-derivatives afford di- and tri-bromonitrobetanaphthol; the bromine atom displaced by NO_2 by this method of treatment, there can be little doubt, is invariably that in the α_1-position.

The authors are of opinion that the intermediate compounds in question are nitro-bromo-keto-derivatives corresponding to the dichloro-keto-compounds of Zincke, and that their formation affords evidence that the elements of nitric acid first become added to the bromonaphthol, thus:—



The theory that the formation of such addition compounds precedes that of nitro-compounds generally appears to afford a satisfactory explanation of a large number of well-known facts which hitherto have remained unexplained. The non-production of nitro-compounds from paraffins and their derivatives, except in a certain very limited number of special cases, appears as the natural consequence of the inability of paraffins to form addition compounds. The theory affords a simple explanation of the formation of nitro-derivatives of *phenols* on nitrating hydrocarbons, to which Nölting has drawn special attention in the case of toluene and orthoxylene (*Berichte*, 1885, 2670; 1888, 3158), for if the addition compound lose HNO_2 instead of H·OH a phenol would result; thus—



An agent that would favour the separation of the elements of water from the addition compound would increase the production of the nitro-compound and diminish that of the phenol; and, as a matter of fact, it is known that when a mixture of nitric and sulphuric acids is used there is less of the phenol derivative produced than when nitric acid alone is employed. A compound such as the addition compound of benzene with nitric acid above represented would obviously be unstable and prone to undergo oxidation; hence it is not difficult to understand that so large an amount of nitrous fume should be produced even on nitrating benzene. The reduction in the amount of such fume, and the improvement of the yield of nitro-derivative effected by adding sulphuric acid, is doubtless attributable to the action already referred to of the acid in promoting the separation of the elements of water; sulphuric acid must be supposed, in fact, in such cases to act not merely as a dehydrating agent in maintaining the nitric acid concentrated, but to exert a specific influence on the course of change. Lastly, the resinous matters often formed in large amount on nitrating

many phenols are, doubtless, products of the interaction of several molecules of the addition compounds, or of the keto-compounds formed from them in the first instance.

The non-production of resinous matters when sulpho-acids are treated with nitric acid so as to form the corresponding nitro-compounds by displacement of the SO_3H group by NO_2, a modification which often makes it possible to prepare nitro-compounds not obtainable by the direct action of nitric acid, is also elucidated by the authors' theory; the addition compound formed in such a case, would very readily break up into sulphuric acid and the nitro-derivative, thus:—

$$:C(OH)\cdot C(SO_3H): + HO\cdot NO_2 = \cdot C(OH)_2\cdot C(NO_2)(SO_3H)\cdot = :C(OH)\cdot C(NO_2): + HO\cdot SO_3H.$$

Discussion.

Mr. Groves said that he had been much struck, when preparing dinitrobenzene from benzene which had been most carefully purified, on observing that a very appreciable quantity of trinitrophenol was produced; the theory of nitration put forward by the authors would fully account for this.

22. "A new method of preparing nitro-derivatives and the use of nitrogen dioxide as a nitrating agent." By Henry E. Armstrong and E. C. Rossiter.

Reference has been made in the foregoing note to the production from the compounds formed by the addition of the elements of nitric acid to the bromo-derivative of betanaphthol of nitro-derivatives of the naphthol *on treatment with alkali*, a bromine atom becoming displaced by NO_2. As in this interaction a bromine atom is removed and an atom of hydrogen is added to the CO group, such a method of treatment obviously is scarcely that best calculated to effect the formation of the nitro-derivative, and, as a matter of fact, the nitro-derivative is not the only product. On treating the addition compound, however, with sulphurous acid, a practically theoretical yield of the nitro-naphthol is obtained; this method appears to be of general application.

The authors have been naturally led to study the action of nitrogen dioxide, NO_2, on unsaturated compounds of various kinds, in the expectation of obtaining addition compounds which by loss of HNO_2 would pass over into nitro-derivatives of the substances treated. They find that such addition compounds are actually obtainable, and that on treatment with alkali and reducing agents, they yield nitro-derivatives. Thus betanaphthol affords as much as 75 per cent. of its weight of nitro-betanaphthol; alphanaphthol behaves similarly.

In some cases, the addition compound is so unstable that it spontaneously decomposes: thus phenol at once yields a mixture of ortho- and para-nitrophenol. The authors propose to study the behaviour of unsaturated compounds generally towards nitric acid and nitrogen dioxide from the point of view indicated in this and the previous note.

23. "Nitrification. Part IV." By R. Warington.

The first section of the paper describes early experiments, made in 1878—84, showing the existence of an agent producing only nitrites, and the means of separating it from soil. It was at first thought that the age of the culture was the factor which determined the loss of the power of producing nitrates, but this idea was negatived by subsequent experiments. Successive cultivation in ammoniacal solutions, made permanently alkaline with disodium carbonate, was found to be a certain method of obtaining a purely nitrous agent. Pasture soil yielded the nitrous agent more readily than arable soil.

The isolation and properties of the nitrous organism are next described. The gelatinous matter which appears under certain conditions at the bottom of old cultures was in 1883 examined microscopically, and found to consist of circular corpuscles imbedded in a zooglœa. In 1886, this jelly was spread on gelatin, but it yielded no nitrifying organism. In 1889, a systematic attempt at the isolation of the organism commenced. Successive cultivations were made in an ammonium carbonate solution, supplied with phosphates, &c., but containining no organic matter. A series of transparent cultures was obtained, containing only nitrites. These cultures were spread on gelatin and agar-agar, the composition of the jelly being made to correspond, as far as possible, with that of a nitrifiable solution. The later cultures yielded on gelatin one organism only, a short bacillus. This and all the other organisms obtained by cultivation on gelatin from nitrified solutions were seeded into both liquid and solid media susceptible of nitrification, but without result. Microscopical examination of the nitrified solutions showed that cocci were abundantly present, but these never appeared on the gelatin cultures.

The first attempts to separate the nitrous organism by the dilution method failed. By substituting an ammonium chloride solution with calcium carbonate for the ammonium carbonate, success was attained in October, 1890, three nitrified cultures seeded with dilutions of 1/10,000, 1/100,000 and 1/1,000,000 giving no growth on gelatin.

The nitrous organism thus obtained oxidises ammonia to nitrous acid and has no effect on nitrites. It produces nitrous acid in solu-

tions of asparagine, milk, urine, and urea. Grown in broth containing calcium nitrate, it does not reduce the nitrate to nitrite. It produces no turbidity or visible change when grown in broth or in any of the other solutions named.

The nitrous organism requires no organic matter for its nutrition; it is apparently capable of assimilating carbon from acid carbonates. The presence of either calcium or sodium acid carbonate distinctly favours nitrification; neutral sodium carbonate greatly hinders nitrification. The proof that carbon is assimilated from carbonates has been furnished by Winogradsky. The energy that is required for the decomposition of a carbonate is apparently furnished by the oxidation of ammonia on nitrogenous organic matter. Calcium acetate (0·25 gram per litre) favours nitrification when only the nitrous organism is present.

The nitrous organism occurs as nearly circular corpuscles, varying from minute points up to nearly 1·0 μ in diameter; these circular organisms stain deeply. It also occurs as oval cocci, the length frequently exceeding 1·0 μ, the ends occasionally more or less truncated.

The remainder of the paper deals with the nitric organism. Results obtained in 1880—81 revealed the existence of an organism which energetically converted nitrites into nitrates, but was apparently unable to oxidise ammonia. In 1886 and 1890, attempts were made to separate the active organism from the 1881 cultures by growths on gelatin and potato; none of the organisms thus separated had any power of oxidising either ammonia or nitrites. Recent results show that the nitric organism develops freely in inorganic solutions containing potassium nitrite, phosphates, &c., especially if supercarbonates are present. Monosodium carbonate, 1—4 grams per litre, exerted a very favourable influence, 6 grams a retarding influence. Disodium carbonate greatly hinders its action.

The nitric organism produces neither nitrites nor nitrates in ammoniacal solutions, even when carbonic acid, or monosodium carbonate, or calcium acetate is supplied. In the absence of ammonia it energetically converts nitrites into nitrates; the presence of ammonia is apparently a great hindrance to its action.

An attempt to isolate the nitric organism by the dilution method failed, but apparently only one other organism (a stout bacillus growing on gelatin) was present in some of the cultures obtained. The stained preparations from these cultures contained an abundance of the minute circular organisms observed in pure cultures of the nitrous organism; the form of the two organisms is thus apparently similar.

The nitrification performed by soil thus appears to be the work of two organisms, one of which oxidises ammonia to nitrite, while the

other oxidises nitrite to nitrate. The first organism is easily separated from the second by successive cultivations in solution of ammonium carbonate. The second is (probably) separated as easily from the first by successive cultivations in solution of potassium nitrite containing monosodium carbonate.

The paper was illustrated by micro-photographs, showing the nitrous organism as developed in ammoniacal solutions, milk and broth; and the nitric organism grown in a solution of nitrite. The photographs were executed by A. Pringle, Esq., and Dr. Bousfield.

Discussion.

Professor Thomson, referring to the method of cultivation on gelatinised silica described by Mr. Warington, said that the account given of the method reminded him of an observation made so far back as 1875: a solution of silica which he had prepared by dialysis had solidified, and he noticed, after a time, that a growth of what he thought was an ordinary mould had appeared on the surface; there could have been nothing present besides the silica, except traces of mineral salts.

Dr. Munro said that he was glad to see that his contention that organic matter was actually prejudicial to the growth of the nitrifying organism was now proved. Referring to the conclusion that two organisms were concerned, one of which converted the ammonia into nitrite, the other extending the oxidation to nitrate, he asked how those cases in which only nitrates were found were to be explained; it very rarely happened, for instance, that in well-waters the ammonia was converted into nitrate with intervention of nitrite. Perhaps two organisms were present, which did their work simultaneously.

Mr. Warington, in reply, said that the two organisms would have no difficulty in acting together in very weak solutions of ammonia.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Transactions of the Sanitary Institute. Vol. XI. Congress at Brighton, 1890. London 1891. From the Council.

University of Nebraska. Fourth Annual Report of the Agricultural Experiment Station of Nebraska. Lincoln, Nebraska, U.S.A. 1891. From the Director of the Station.

Smithsonian Miscellaneous Collections:—

708. The Toner Lectures. Lecture X. A Clinical Study of the Skull, by H. Allen.

741. Index to the Literature of Thermodynamics, by A. Tuckerman.

764. The Correction of Sextants for Errors of Eccentricity and Graduation, by J. A. Rogers. Washington 1890.

From the Institution.

II. *By Purchase.*

Anleitung zur chemischen Analyse organischer Stoffe, von G. Vortmann. II Hälfte. Leipzig und Wien, 1891.

Transactions of the Royal Society of Edinburgh. General Index to Vols. 1—34 (1783—1888). Edinburgh 1890.

The Metallurgy of Steel, by H. M. Howe. New York, 1891.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE NEXT BALLOT.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

Belbin, Tom St. John,

12, Bolton Mansions, South Kensington.

Consulting Brewer, Analyst, &c. Four years student at Firth College under Professor Williams. Two years Chemist, &c., at the Rutland Brewery, and one and a half at the Plant Brewery, Doncaster; six years Consulting Brewer and Analyst.

Henry P. Harris. Thomas Jenner.
Wm. Gregory. Bedo Hobbs.
Henry L. Dampier. *Basil Pemdarne Wigan.*

Brown, Edward,

32, Courlandsky Street, St. Petersburg.

Chemist to the Russian Steam Oil Mill Company here; a thorough course of Chemistry at the Bradford Technical College and School of Mines, S. Kensington; two years Manager of a chemical works at Cleckheaton, Yorks; and two years Analytical Chemist here in St. Petersburg.

Charles Wood. G. W. Slatter. C. Rawson.
Thorp Whitaker. *Sidney Wood.*

Congdon, Ernest A., Ph.B.,

Lehigh University, S. Bethlehem, Penn., U.S.

Chemist. Instructor of Chemistry at Lehigh University three years; now Professor of Chemistry at the Drexel Institute, Philadelphia, Penn.

Edw. Gudeman. Charles F. Chandler. Elwyn Waller.
Jas. S. C. Wells. Hermann T. Vulté.

Dreaper, W. Porter,

1, Ceal Villas, Ceal Road, Enfield.

Experimental Chemist. Three years student at City and Guilds of London Technical College, Finsbury. Hon. Demonstrator during

last year, and holding certificate of college, and 1st prize, 1st and 2nd years. For the last three years in charge of Messrs. Grant & Co.'s Ponder's End Works Laboratory. Associate of Institute of Chemistry (by exam.).

Otto Hehner. R. Meldola. Gerald T. Moody.
Henry E. Armstrong. Holland Crompton.

Duncan, William,

10, Plough and Harrow Road, Edgbaston, Birmingham.

Brewer's Chemist. In October, 1885, obtained Ackroyd Scholarship, value £25, for two years, at the Yorkshire College, Leeds. Course of Study:—Chemistry, Mathematics and Physics; working in the Chemical and Physical Laboratories under Professor Smithells. In 1887 obtained Senior Brown Scholarship, value £35, for two years. Continued with similar course of study. In June, 1889, passed examination of the Institute of Chemistry, held at Owens College. Since October, 1889, up to the present time, have held a situation in connection with a brewery. Specialising in this branch of Chemistry.

Arthur Smithells. Charles H. Bothamley. Herbert Ingle.
Walter M. Gardner. A. Battye Knaggs.

Gregory, Alfred John,

The Bays, Knight's Hill, West Norwood, S.E.

Bachelor of Medicine, B.S., M.R.C.S., &c. Reason for wishing to become a Fellow is my keen interest in Chemistry in its relations to Physiology and Medicine.

C. Meymott Tidy. Frederic Jas. M. Page.
George Robertson. L. Gowdon Paul.
A. H. McConnell.

Holloman, Frederick R.,

Sugar Refinery, Rawcliffe Bridge, Selby.

Chemist and Works Manager to Mr. James Duncan, Rawcliffe Bridge, Selby. Student Assistant under Mr. J. A. R. Newlands, F.I.C., F.C.S., 1879—83; Assistant Chemist at Starch Sugar Works, Newcastle-under-Lyme, 1883—84; Assistant Chemist at the Stanhope Water Company, London, 1884—85; Assistant Chemist at the Clyde Wharf Sugar Refinery, 1885—86; Chief Chemist to Messrs. L. Cowan & Sons, Soap Works and Sugar Refinery, 1886—90.

James Duncan. John A. R. Newlands. Arthur R. Ling.
B. E. R. Newlands. *Watson Smith.* *D. A. Louis.*
Thos. Tyrer.

Knowles, John,

Northwich, Cheshire.

Manufacturing Chemist. Eleven years' analytical work, six years Manager Chemical Works, lecturing in Chemistry under Science and Art and City and Guilds in Chemical Technology.

Fredc. H. Bowman. J. Carter Bell. Rowland Williams.
H. Grimshaw. *Wilfred Irwin.* *William Thomson.*

Leeds, Frank H.,

29, Bouverie Road, Stoke Newington, N.

Analytical and Consulting Chemist. Associate of the Institute of Chemistry. Three years assistant in laboratory of Tar Works of Gas Light and Coke Co., Beckton. One year Chemist to J. Kidd & Co., Printing Ink Manufacturers.

R. J. Friswell. A. G. Green. T. A. Lawson.
W. S. Simpson. *T. Cooksey.*

Macfie, Robert Andrew Scott,

Rowton Hall, Chester.

Student of Chemistry in the University of Edinburgh. Holding the degree of Bachelor of Arts (Cantab.), with honours in Science, having studied Chemistry in Cambridge for three years, at Göttingen, and in Edinburgh; specially interested in the technical chemistry of sugar.

Alex. Crum Brown. James Walker.
M. M. Pattison Muir. S. Ruhemann.
J. Augustus Voelcker. Lyon Playfair.

Michael, Arthur,

Torwood, Bonchurch, Isle of Wight.

Member of the American National Academy. Author of numerous communications published in the *American Chemical Journal*, the *Berichte*, and the *Journal für praktische Chemie.*

Henry E. Armstrong. F. R. Japp. R. Meldola.
John M. Thomson. *J. H. Gladstone.* *W. H. Perkin.*

Mitchell, Thomas,

C/o E. Mitchell, Crossmount, Bridgend, Perth, N.B.

Mining Engineer and Assayer. Studied Metallurgy and Mineralogy, and did practical Laboratory work under Professor Humboldt Sexton, Glasgow. Chemistry and practical Laboratory work, Technical College, Dundee, under Dr. Andrew Thomson and the late Professor Carnelley. Natural Philosophy under Professor Tait, Edinburgh, Held the position of Superintendent in connection with Silver

Mining in America, and have prospected in different parts of the United States.

A. Humboldt Sexton. Thos. A. Cheetham.
Andrew Thomson. Thomas S. Murray.
David Ferrier.

Mousley, Harry Joseph Marston,
Kingsbury, Portland Road, Edgbaston.

Brewer's Chemist and Lecturer to Students in Brewing. Experience:—Three years in Laboratory (Chemical) under Professor Woodward, B.Sc. Three years in Laboratory (Metallurgical) under Professor Hiorns. Five years (from age of 15 to 20) at Messrs. Chance Bros.' Alkali Works, as Laboratory Assistant. 13 months at Messrs. Peyton and Son, Chemical Works, as Head Chemist. Six months with Mr. Faulkner, Consulting Brewer (three months at Showell's Brewery, three months at Mitchell's Brewery). Examinations in the Science and Art:—Second Class: Practical and Theoretical Organic Chemistry. First Class: Magnetism and Electricity. Electro-metallurgy, Geology, Mineralogy. First Class (Honours): Practical Chemistry, Inorganic, and Metallurgy. Practical and Second Class Theoretical, &c., &c.

A. B. Griffiths. Harold Follows. Alexander Hay.
Alexander M. Chance. *C. Schorlemmer.* *Thomas A. Pooley.*
W. Lawrence Gadd. *E. Cleminshaw.*

Notter, James Lane,
Leigh Grange, Woolstone, Southampton.

Professor of Military Hygiene at the Army Medical School, Netley. M.A., M.D., University of Dublin. Professor of Hygiene and Lecturer on Chemistry, Netley. Various Reports and Analyses for War Office. See *Army Med. Depart. Reports*, 1887—88; also various Analyses. See *Sanitary Record*, 1880—81, &c., &c.

J. Emerson Reynolds. Thos. Stevenson. W. H. Corfield.
T. W. Shore. W. B. Randall.

Perkin, F. M.,
Heriot Watt College, Edinburgh.

Student of Chemistry. Two years student School of Mines, South Kensington; one year research student Heriot Watt College; Author of paper on "Some Derivatives of Piperonyl" (*Trans. Chem. Soc.*).

Henry E. Armstrong. F. Stanley Kipping. T. E. Thorpe.
Chapman Jones. A. E. Tutton. *W. P. Wynne.*
John M. Thomson.

Rhodes, Edward,

Holly Bank, Frodsham, Cheshire.

Analytical Chemist at Phosphate Works. No published contributions to Chemical Science, but read a paper on "Phosphates" before the Owens Coll. Chemical Society, in 1882. Educated in Science, Chemistry, Physics, &c., at the Manchester Grammar School, 1871 to 1875. 1875 and 1876 devoted whole time to study of Chemistry, inorganic and organic, at Owens College. 1876 to 1880 Assistant Chemist at Thos. Vickers & Sons' Chemical Works, Manchester. 1880 to present date Head Chemist at T. Vickers' Phosphate Works, Widnes.

Francis Jones.	H. E. Roscoe.	W. Carleton Williams.
L. T. O'Shea.	R. L. Taylor.	Wilfred Irwin.
Edward Jackson.	Gibson Dyson.	Alfred Smetham.

Rossiter, Edmund Charles,

39, Brook Green Road, Hammersmith.

Honorary Demonstrator, Chemistry Department, Central Institute (City Guilds). Three years student at the City and Guilds of London Institute, Central Institution; and Associate of the Institute in Chemistry.

Henry E. Armstrong.	W. P. Wynne.	Gerald T. Moody.
Henry A. Miers.	W. J. Pope.	Harold G. Colman.

Shields, John,

The Byers, Bathgate, N.B.

Student of Physical Science. Bachelor of Science of the University of Edinburgh; Doctor of Philosophy of the University of Strassburg (Dissertation: "On the Reduction of Phenylparaconic Acid and Phenylbutyrolactone"); Medallist in Chemistry Class, University of Edinburgh; Joseph Black Prizeman, University of Edinburgh (Dr. Gunning's Foundation); recommended by the University of Edinburgh to the Royal Commissioners for the Exhibition of 1851 for a Scholarship in Physical Science.

Alex. Crum Brown.	James Walker.	Thomas S. Murray.
Hugh Marshall.	Leonard Dobbin.	*W. H. Perkin, junr.*

Solomon, Frank O.,

North Eastern County School.

Professor of Agriculture and the allied Sciences. Studied Chemistry two years under Dr. J. M. H. Munro, and took first place in Theoretical Chemistry, also in Laboratory work. Certificated member of the College of Agriculture, Downton. Holder of First Class

Certificate of Highland and Agl. Society (Examiner in Chemistry, Dr. Aitken, Edinburgh.) Lecturer for various Chambers of Agriculture in the neighbourhood on the Science and Practice of Agriculture.

E. D. Walrond. John Wrightson. John M. H. Munro.
Charles Hy. Corbett. *W. F. K. Stock.* *John J. Pilley.*

Taylor, John,

15, Lucius Street, Torquay.

Analytical Chemist. Analytical and Consulting Chemist to Messrs. Morris and Callard, Chemical Manufacturers, Ammanford, South Wales.

Jno. Wiltshire. W. A. H. Naylor. Thos. Tyrer.
Geo. Bult Franc's. *L. W. Hawkins.*

Tetley, Frederick,

3, Mannville Terrace, Horton Road, Bradford.

Analytical Chemist. For five years Assistant to Mr. C. Rawson, Consulting Chemist, Bradford, and the past 15 months Chemist to Messrs. Wm. Grandage & Co., Dyers, Bradford.

C. Rawson. G. W. Slatter. Thorp Whitaker.
R. Elliot Steel. *F. M. Rimmington.*

Weber, Dr. Otto Carl,

Rectory Road, Crumpsall, Manchester.

Analytical Chemist. Studied for three years at the Royal Polytechn. School at Stuttgart under v. Fehling, and subsequently for 1½ years at the University at Heidelberg under Bunsen and Kopp, where I took my degree Ph.D. Since then I have been engaged in analytical and manufacturing chemistry as applied to the manufacture of pigment and coal-tar colours, dyeing and printing. Two large colour works in Austria and Switzerland have been built by me, and the manufacture of aniline pigments has been, to a large extent, originated by me. Appended are some of the papers I contributed to various scientific Journals.

J. Carter Bell. Percy Carter Bell. Fredc. H. Bowman.
Rowland Williams. H. Grimshaw. *Otto Hehner.*
Thos. Tyrer. *Charles Watson.*

Williams, Seward W.,

East Orange, New Jersey, U.S.A.

Superintending Chemist, Seabury Pharmacal Laboratories. Graduated as Ph.C., University of Michigan, 1881. Assistant in Qualitative Chem. Analysis, Ann Arbor Laboratories, 1881—82. Associate

Editor *Drug News and American Pharmacist*, 1883—85. Chemist to Seabury and Johnson, 1885—91. Member Am. Pharm. Assn., American Chemical Society, N.Y. State Pharm. Assn. and New York College of Pharmacy.

Joseph F. Geisler.	Albert B. Prescott.	Wm. D. Crumbie.
Alfred Hy. Mason.	*J. H. Wainwright.*	*Elwyn Waller.*
H. Helbing.	*Thos. Tyrer.*	

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Issued 13/6/1891.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 99. Session 1891–92.

June 4th, 1891. Mr. William Crookes, F.R.S., Vice-President, in the Chair.

Messrs. F. Stanley Kipping and Mr. Ernest F. Hooper were formally admitted Members of the Society.

Certificates were read for the first time in favour of Messrs. William A. S. Calver, 45, Barrington Road, Brixton, S.W.; John William Heap, 33, Upper Gloucester Place; Robert Lennox, 3, Inverness Terrace, Putney, S.W.; Rudolf Laurentz Leffler, 21, Havelock Street, Sheffield; Charles K. Scott, 26, Pigott Street, Limehouse, E.; Thomas Stephenson, Bellasis Road, Byculla, Bombay; Henry White, 8, Brown Street, Masboro', Rotherham.

The following papers were read:—

24. "The molecular refraction and dispersion of various substances in solution." By Dr. J. H. Gladstone, F.R.S.

The paper is a continuation of that laid before the Society in March last, and deals entirely with solid and gaseous substances that have been dissolved in water or other liquids for examination.

The results are given in several tables. It cannot be expected that there should be anything like the same accordance between the experimental and calculated numbers as is usually found in the case of pure liquids, as in weak solutions the experimental error is greatly multiplied. Nevertheless, in the case of organic compounds, the agreement is frequently very close. Terpene hydrate and terpilene dihydrochloride appear as saturated compounds, and so do camphor and its derivatives; but benzyl camphor, $C_{17}H_{22}O$, and benzal camphor,

$C_{17}H_{20}O$, substances recently prepared by M. Haller, give results, especially in dispersion, which are far in excess of what might have been anticipated. The sugar group presents some peculiarities. Cane sugar seems to show a refraction, and especially a dispersion, rather smaller than theory. Milk sugar, dextrose, and glucose are fairly accordant with theory; while mannitol, on the other hand, seems a little high in refraction.

Hydrogen chloride, bromide and iodide give figures for the molecular refraction and dispersion much higher than the sum of the hydrogen and the halogen as determined from the paraffin compounds, and the values rise as the dilution becomes greater. Peculiarities analogous to this had previously been discovered by Perkin in regard to their magnetic rotation. Selenious and selenic acids, like the analogous sulphur compounds, afford optical values vastly less than what would be expected from the known values of their constituents. Metaphosphoric acid does the same.

The data relating to solutions of salts and alkalis, including compounds of aluminium, ammonium, barium, calcium, cerium, chromium, didymium, iron, iridium, lead, lithium, lanthanum, magnesium, potassium, silver, sodium and tin. It will afford material for a revision of the refraction equivalents of the different metals, and of the electro-negative elements with which they are combined. They will also furnish additional means for determining the dispersion equivalents. Among the points noted are the following:—Ammonia, in strong contrast with the hydrides of chlorine, bromine and iodine, appears to be uniform in its optical properties, whatever the strength of the solution; it agrees with what would be expected from theory. The refraction equivalents of cerium, didiymium and lanthanum are deduced from their salts at about 12·4, 16·4 and 15·5 respectively. The chlorates, bromates and iodates are sufficiently represented to give an idea of their optical characters. At first sight, it would appear that the addition of 3O to the haloid salts causes an inadequate increase of the molecular refraction, and a slight actual decrease in the molecular dispersion. But this probably arises from the fact that the haloid salts themselves, when dissolved in water, give a somewhat excessive value. The molecular refraction for ClO_3 in its salts dissolved in water comes out at about 18·3, that for BrO_3 at 24·9 and for IO_3 at 33·8.

Discussion.

Dr. Perkin remarked that there was a close agreement between Dr. Gladstone's conclusions and those which he had arrived at from

the study of magnetic rotatory power. The very high values afforded by the elements sulphur and phosphorus, in comparison with the values deduced for these elements from sulphuric and phosphoric acids, were very striking. The magnetic rotatory power of caustic soda was also very high.

Dr. GLADSTONE, in the course of remarks on Dr. Perkin's comments, said that it was particularly noteworthy that sulphur retained its high value in carbon bisulphide.

25. "The nature of solutions as elucidated by a study of the densities, heat of dissolution and freezing points of solutions of calcium chloride." By S. U. Pickering.

The curves representing these properties were examined in the same way as those representing various properties of sulphuric acid, and similar conclusions are drawn in the two cases, namely, that definite changes of curvature occurs at certain points which are the same, whatever property is examined, and which coincide, in all cases where such a coincidence can be ascertained with certainty, with simple molecular proportions of the salt and water; and, consequently, that these changes represent the existence of hydrates in solution. The simplest hydrates indicated in the present case consist of $CaCl_2$ with 6, 7 and $8H_2O$; more complex hydrates exist also, as in the case of sulphuric acid.

26. "Note on a recent criticism by Mr. Sydney Lupton of the conclusions drawn from a study of various properties of sulphuric acid solutions." By S. U. Pickering.

Mr. Lupton (*Phil. Mag.*, **31**, 418) applies a single parabolic equation to a portion of one of the author's sulphuric acid density curves, where a change of curvature was supposed to exist, and shows that it represents the results accurately if the experimental error is of a certain magnitude. This magnitude, however, is between 1000 and 10,000 per cent. greater than the ascertained magnitude, and the equation, moreover, represents all the errors of like signs as being grouped together. Such a representation cannot disprove the existence of the particular change of curvature under investigation, still less that of the 101 others shown in the various curves examined by the author. The hydrate on which Mr. Lupton considers that his investigation throws "very grave suspicion" happens to be the one which the author has isolated in the crystalline condition.

Discussion.

Professor Ramsay doubted the validity of Mr. Pickering's methods of differentiating his curves. His own experience was that it was impossible to obtain results nearer than 2 or 3 per cent. to the truth, with a curve drawn as carefully as possible, and a straight steel-edge laid along it to obtain tangents. Mr. Pickering, on the other hand, pursued a much more crude method, viz., he directly connected his experimental points by straight lines, and took the slopes of such lines as the tangents to his curves. This obviously did not eliminate any experimental error, but rendered it more marked.

Dr. Armstrong said that he had no desire to intervene in the discussion which had arisen as to the validity of Mr. Pickering's method. It appeared to him, however, that Mr. Pickering's conclusions were in many respects open to question from a chemist's point of view; he thought, in fact, that Mr. Pickering both proved too much and was illogical. Prepared as the speaker was to believe in the existence of hydrates in solution, he could not imagine that so large a number as was suggested would arise, or that the 102 breaks in the sulphuric acid curves, for example, could possibly be interpreted as evidence of as many distinct hydrates. There was no independent evidence to support such a conclusion.

Then he thought Mr. Pickering was illogical, because he interpreted all the breaks as indicative of hydrates, notwithstanding that he asserted—doubtless, with justice—that both water and sulphuric acid in the pure state consisted of complex molecules: surely in this case, as change would set in at either end of the curve, it must be impossible to say which of the breaks are to be regarded as indicative of change in the composition of the complex molecules of acid and water respectively, which are due to the formation of hydrates consisting of simple water and acid molecules, and which are due to the formation of hydrates, say, of simple water and complex acid molecules.

With regard to Mr. Pickering's contention that Mr. Lupton must be wrong, because the latter had dealt with the part of the curve which included that hydrate which of all others was the best characterised hydrate of sulphuric acid—a hydrate that he had prepared before them in the room—Dr. Armstrong said that, from experiments which were being carried on in his laboratory, he was inclined to believe that the said hydrate probably did not begin to form in solution until the temperature sank to within a few degrees of its point of fusion: it might well be therefore that it was not present in the solution to which Mr. Lupton's conclusions related.

The more the speaker studied these questions experimentally, the more inclined he became to think that changes of composition, whenever they occurred, were indicated on curves drawn directly to represent the experimental results.

Dr. Morley said that it appeared to him that, even if Mr. Pickering was correct as to the number and position of breaks in the curves, it by no means followed that he had proved the existence of the particular hydrates suggested. A break in the curve should indicate that some new hydrate had just begun to form, but need not show what that hydrate was. Thus it was probable the hydrate $CaCl_2 8H_2O$ would begin to form before the entire liquid contained a percentage of calcium chloride corresponding to that formula; and when the liquid had attained that composition, it might be expected to contain, besides the hydrate $CaCl_2 8H_2O$, also higher and lower hydrates, such as $CaCl_2 9H_2O$ and $CaCl_2 7H_2O$.

Professor Rücker, while fully admitting that the concordance of the numbers obtained by Mr. Pickering from observations on different physical properties of the solutions might fairly be urged in his favour, thought it important that the agreement between results all of which depended on the application of the same method should not be regarded as conclusive evidence in its favour if it were otherwise open to grave doubt.

In reality, Mr. Pickering's results were obtained, not by calculation, but by a method of observation and experiment applied to curves, which themselves represented the results of other experiments. The instrument used was a flexible ruler. It was admitted that the curves had to be specially drawn and the scale of the coordinates carefully chosen, if the results were to be satisfactory, and it was difficult to believe that the conclusions arrived at did not in large measure depend on the details of this preliminary adjustment.

At all events, as in the case of all other experimental methods, the final test of validity is whether concordant results are obtained by different observers, and it was therefore important that those who had personally tested it should give the results of their experience.

The speaker had himself gone over Mr. Pickering's work in the case of one of the sets of observations on the densities of dilute sulphuric acid of different strengths, and he could bear witness to the care with which the curves were drawn. Nevertheless, the conclusion he arrived at was precisely similar to that which Professor Armstrong had expressed.

In the case of the more striking changes in direction and curvature which were clearly visible in the original curve, the various differential curves did not add much to the information it supplied. On the other hand, he thought that the evidence afforded by these

secondary curves of changes of curvature, which could not otherwise be detected, was of the most untrustworthy character.

The assumption seemed often to be made that, because the results of experiments were more closely represented by two curves than by one, there must be a discontinuity, which was evidence of some physical change. That this conclusion might be fallacious is evident from the fact that, if a sufficient number of discontinuities were admitted, the results of experiment might be represented graphically with absolute fidelity.

His experience of the method would lead him to doubt any conclusions based upon it alone and not supported by independent evidence. It became untrustworthy just when it professed to become useful, by supplying information which could not otherwise be attained.

Mr. Pickering said that Mr. Lupton's equation represented the rate of change of the densities as a straight line, while the figure which the actually observed rate of change formed was as different from a straight line as could well be imagined (*C. S. Trans.*, 1890, 80). The straight line might be regarded as fitting a greater or smaller portion of this experimental figure, according to the latitude allowed to experimental error. In order that it should fit that portion of the figure which Mr. Lupton said it did, the latitude to be allowed would have to be 10 to 100 times greater than that for which there was any warrant. This, he considered, was not allowable. The figures here referred to (and exhibited at the meeting) were the first differential figures (rate of change) deduced *directly* from the determinations themselves; the question, therefore, of the accuracy attainable in differentiating a graph, raised by Professor Ramsay, did not apply to them.

It seemed somewhat rash of Professor Armstrong to hold that a particular hydrate ($H_2SO_4 4H_2O$) did not exist in solution at moderately high temperatures, because from a study of one property he had recognised it at low temperatures only, especially as it was from his own results at high temperatures that the speaker had been led to search for it, and finally to isolate it, at low temperatures. The multiplicity and complexity of the hydrates indicated must, no doubt, endanger the acceptance of his conclusions amongst chemists; but without reason, he thought, for we are at present in the dark as to the nature of liquid molecules (see *loc. cit.*, pp. 124, 129). He would be perfectly ready to accept any other explanation of the changes with weak solutions than that of their being due to hydrates, but he considered that we have at present no evidence in favour of any other view, or of their being due to changes in the aggregation of the solvent molecules, while the fact that they are precisely similar to the changes with strong solutions which occur at simple

molecular proportions forces us to attribute them to the same cause as the latter, until some evidence to the contrary be forthcoming. He had already alluded to the question raised by Dr. Morley, as to why the existence of a hydrate should cause a change of curvature at exactly the strength of the solution corresponding to it (*loc. cit.*, p. 138), but he had left that question to those who had sufficient mathematical abilities do deal with it. Mendeléeff, however, appeared to consider that no exception could be taken on that score (*C. S. Trans.*, 1887, p. 779).

The fact mentioned by Professor Rücker, that a flexible spring could be made to fit any complicated curvilinear figure by fixing it in position by a sufficient number of pins, did not appear to disprove the existence of definite changes of curvature in the figure; for the forces acting on the spring between any two given pins would be different from those acting on it between any other two; and, consequently, the form of the different portions of the spring would be represented by different equations, that is, there would be changes of curvature. He did not see how the position of these changes of curvature could be said, on either theoretical or practical grounds, to depend on the flexibility of the spring used; for he believed he was correct in saying that all springs, when acted on by forces of a similar nature, assumed similar forms, and any difference in the degree of curvature due to a difference in flexibility might be counteracted by a difference in the magnitude of the forces applied. In practice, he had used numerous springs of very different degrees of flexibility, without finding any difference in the position of the changes of curvature indicated. It seemed scarcely correct to say that the application of a flexible lath to a curvilinear figure led to different results in different hands, because Mendeléeff's conclusions respecting the densities of sulphuric acid differed from the speaker's; for Mendeléeff had an altogether insufficient number of experimental points at his disposal, and, as far as could be judged, did not use a flexible lath at all in examining them. The question as to whether a lath could or could not be used in locating changes of curvature which were not apparent to unassisted inspection might be most easily settled by submitting a fictitious series of determinations, calculated from sundry different equations, to examination with a lath, and ascertaining whether the position of the changes of curvature found coincided with those at which the equations had been changed. He was quite ready to submit his process to this crucial test.

27. "Ethylic $\alpha\alpha'$-dimethyl-$\alpha\alpha'$-diacetylpimelate and its decomposition products." By F. Stanley Kipping, Ph.D., D.Sc., and J. E. Mackenzie, B.Sc.

When diacetylpentane is reduced with sodium and moist ether it is converted into dimethyldihydroxyheptamethylene (*cf.* Kipping and Perkin, *C. S. Trans.*, 59, 214), according to the equation

$$CH_2<\begin{matrix}CH_2\cdot CH_2\cdot CO\cdot CH_3\\ CH_2\cdot CH_2\cdot CO\cdot CH_3\end{matrix} + 2H = CH_2<\begin{matrix}CH_2\cdot CH_2\cdot C(OH)\cdot CH_3\\ CH_2\cdot CH_2\cdot C(OH)\cdot CH_3\end{matrix}.$$

As it seemed probable that other 1 : 7-diketones would behave in a similar manner, the authors have prepared $\alpha\alpha'$-dimethyl-$\alpha\alpha'$-diacetylpentane by the method described below. The action of reducing agents on this diketone is now being investigated by one of them, but, as a considerable amount of work has yet to be done on the subject, they describe in the present paper the preparation and properties of dimethyldiacetylpentane and of various other compounds obtained in the course of the research.

Ethylic $\alpha\alpha'$-dimethyl-$\alpha\alpha'$-diacetylpimelate,

$$CO_2Et\cdot CMeAc\cdot[CH_2]_3\cdot CMeAc\cdot CO_2Et,$$

is formed in considerable quantities when ethylic sodiomethylacetoacetate (2 mols.) is treated with trimethylene bromide (1 mol.) in absolute alcoholic solution; it is a colourless oil boiling at 233—235° under a pressure of 50 mm., and it combines readily with phenylhydrazine (2 mols.) yielding a reddish-yellow *dihydrazone*, which has the composition $C_{29}H_{40}N_4O_4$. On boiling with alcoholic potash the ethereal salt is readily decomposed, the principal products being $\alpha\alpha'$-dimethyl-$\alpha\alpha'$-diacetylpentane, $\alpha\alpha'$-dimethyl-α-acetylcaproic acid, and $\alpha\alpha'$-dimethylpimelic acid.

$\alpha\alpha'$-Dimethyl-$\alpha\alpha$-diacetylpentane,

$$CH_3\cdot CO\cdot CHMe\cdot[CH_2]_3\cdot CHMe\cdot CO\cdot CH_3,$$

is a colourless liquid boiling at 202—204° under a pressure of 150 mm.; when treated with hydroxylamine it is converted into a crystalline *dioxime*, $C_{11}H_{22}N_2O_2$, which melts at 93—94°.

$\alpha\alpha'$-Dimethyl-α-acetylcaproic acid,

$$CH_3\cdot CO\cdot CHMe\cdot[CH_2]_3\cdot CHMe\cdot COOH,$$

is a colourless oil boiling at 226—228° under a pressure of 70 mm., seemingly with slight decomposition. The *silver* salt, $C_{10}H_{17}O_3Ag$, *ethylic* salt, $C_{12}H_{22}O_3$, *methylic* salt, $C_{11}H_{20}O_4$, and the *hydroxime*, $C_{10}H_{19}NO_3$, are described.

$\alpha\alpha'$-Dimethylpimelic acid, $CO_2H\cdot CHMe\cdot[CH_2]_3\cdot CHMe\cdot CO_2H$, separates from light petroleum in well-defined crystals, melts at 80—81°,

and is readily soluble in most ordinary solvents. The *silver* salt, $C_9H_{14}O_4Ag_2$, and the *barium* salt, $C_9H_{14}O_4Ba$, were prepared.

Ethylic-αα'-dimethylpimelate, $COOEt{\cdot}CHMe{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}COOEt$, is formed in the place of ethyl dimethyldiacetylpimelate when trimethylene bromide is treated with ethyl sodiomethylacetoacetate in alcoholic solution, the alcohol employed being not quite anhydrous; it is a colourless oil boiling at 190—191°, under a pressure of 80 mm.

28. "Volatile platinum compounds." By W. Pullinger.

At Professor Lothar Meyer's suggestion, the author has further studied the volatile compounds of platinum with chlorine and carbon monoxide described by Schützenberger, with the object, if possible, of determining their vapour density. He describes their behaviour when heated in various gases; as they do not completely volatilise, even in carbonic oxide, he was unsuccessful in accomplishing his object.

In preparing the compounds, he has obtained a novel compound of the formula $PtCl_6C_2O_2$ as a non-volatile, yellow, crystalline solid, easily soluble in water, and recoverable apparently unchanged from the solution. Liquid carbonyl chloride at 100° is found to act as a solvent of Schützenberger's compounds, depositing them on cooling in large crystals.

The author has prepared the compound $PtBr_2CO$ by heating platinous bromide in an atmosphere of carbonic oxide; apparently it is the only product even when excess of the gas is used. It crystallises in well-defined needles melting at 177°, and volatilising with extreme difficulty, even in an atmosphere of carbonic oxide.

Directions are given for the preparation of platinic bromide and iodide, from which it appears that platinum sponge readily dissolves when merely boiled with either a solution of bromine in bromhydric acid or of iodine in iodhydric acid.

Discussion.

Dr. Collie mentioned, as an instance of a volatile metallic derivative, that he had recently had occasion to notice that the copper derivative of the double ketone diacetylmethane, $(Ac_2CH)_2Cu$, was volatile.

At the next meeting, on June 18th, there will be a ballot for the election of Fellows, and the following papers will be read:—

"The action of sulphuric acid on dehydracetic acid." By Dr. Collie.

"The refractive power of certain organic compounds at different temperatures." By Dr. W. H. Perkin, F.R.S.

"The formation of salts—a contribution to the theory of electrolysis, and of the nature of chemical change in the case of non-electrolytes." By Henry E. Armstrong.

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Issued 3/7/1891.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 100. Session 1891-92.

June 18th, 1891. Professor A. Crum Brown, F.R.S., President, in the Chair.

Mr. F. J. Bloomer was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. William P. R. Newlands, Rosa, North-West Province, India; Laurence Priestley, Forest View, Noel Street, Nottingham; Thomas Armistead Ward, Preston Road, Blackburn.

The following were elected Fellows of the Society:—Tom St. John Belbin; Edward Brown; Ernest A. Congdon, Ph.B.; W. Porter Dreaper; William Duncan; Alfred John Gregory; Frederick R. Holloman; John Knowles; Frank H. Leeds; Robert Andrew Scott Macfie; Arthur Michael; Thomas Mitchell; Harry Joseph Marston Mousley; James Lane Notter, M.D.; F. M. Perkin; Edward Rhodes; Edmund Charles Rossiter; John Shields; Frank O. Solomon; John Taylor; Frederick Tetley; Dr. Otto Carl Weber; Seward W. Williams.

The following papers were read:—

29. "A note on some interactions of dehydracetic acid." By J. Norman Collie, Ph.D., F.R.S.E., University College, London.

During the last six months the author has been working with large quantities of dehydracetic acid, and he finds that several important reactions of this interesting substance have hitherto escaped notice.

In its preparation, by passing ethylic acetoacetate through a red-hot tube, it is stated that alcohol is formed; the author finds that large

quantities of ethylene gas and acetone are produced as well. He also finds that dehydracetic acid is volatile to a considerable extent with steam, and is also decomposed by boiling with water to a small extent into carbon dioxide and dimethylpyrone:

$$C_8H_8O_4 + H_2O = C_7H_8O_2 + CO_2 + H_2O.$$

In the evaporation, therefore, of a solution of the acid a large quantity of the acid is lost. This decomposition into dimethylpyrone is effected far more readily if the acid is boiled with strong chlorhydric acid; if 50 grams are boiled with the ordinary fuming acid, in about half an hour the whole is converted into carbon dioxide and a soluble compound of dimethylpyrone with hydrogen chloride. This hydrochloride crystallises from strong solutions in magnificent groups of tabular crystals. Feist states (*Annalen*, **257**, 253) that chlorhydric acid is almost without action on dehydracetic acid.

The barium salt of dehydracetic acid seems to be not a salt of the compound $C_8H_8O_4$, but of the true tetracetic acid, $C_8H_{10}O_5$, and has the formula $(C_8H_9O_5)_2Ba$.

A curious copper salt has been obtained. If dehydracetic acid be added to a solution of copper acetate in a large excess of ammonia, on allowing to stand, a pink, insoluble salt separates. This salt is very stable, and is not decomposed even when boiled with sulphuretted hydrogen; but if chlorhydric acid is added it is at once decomposed and dehydracetic acid is re-formed.

The formula of the salt seems to be $C_{24}H_{25}O_9N_3Cu$. Such a salt could be produced according to the following equation:—

$$3C_8H_8O_4 + 3NH_3 + Cu(C_2H_3O_2) = C_{24}H_{25}O_9N_3Cu + 3H_2O + 2C_2H_4O_2.$$

30. "The lactone of triacetic acid." By J. Norman Collie, Ph.D., F.R.S.E., University College, London.

In a paper which the author communicated to this Society some short time ago (Trans., 1890, 189) on the constitution of dehydracetic acid, he pointed out that if the formula which he proposed for dehydracetic acid were the correct one, it would then be the *δ-lactone of tetracetic acid*. The following list was then given, which was intended to show the connection between the condensed acids formed from acetic acid:—

$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}COOH$, tetracetic acid.
$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}COOH$, triacetic acid.
$CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOH$, diacetic acid.
$CH_3{\cdot}COOH$, acetic acid.

At that time no acid corresponding to triacetic acid was known. Since then the author has, however, been able to obtain the lactone of this acid by the action of 90 per cent. sulphuric acid on dehydracetic acid at a temperature of 130—135° C. :—

$$C_8H_8O_4 + H_2O = C_6H_6O_3 + C_2H_4O_2.$$

It crystallises from water in fine needles, m. p. 183—189° (corr.).

The properties of this new lactone resemble those of dehydracetic acid. It does not form a stable ammonium salt, for, on evaporation of a solution of the acid in ammonia over sulphuric acid *in vacuo*, a certain quantity of the acid results.

When boiled with acids or water it yields carbon dioxide and acetyl acetone, resembling dehydracetic acid and diacetic acid in this respect :—

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}COOH = CO_2 + CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_3.$$

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}COOH = CO_2 + CH_3CO{\cdot}CH_2CO{\cdot}CH_3.$$

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOH = CO_2 + CH_3CO{\cdot}CH_3.$$

When warmed with strong solution of caustic soda, acetone and acetic acid are produced.

With bromine a mono-substituted bromine derivative is formed (m. p. 200—205°) :—

$$C_6H_6O_3 + Br_2 = C_6H_5BrO_3 + HBr.$$

If treated with hydroxylamine an hydroxime is formed, crystallising in long needles, m. p. 230—231° (corr.).

And finally, if the ammonium salt is heated a nitrogen compound is produced, which is either a pyridine or pyrrol derivative, as it does not give any ammonia when heated with caustic soda :—

$$C_6H_6O_3 + NH_3 = C_6H_7NO_2 + H_2O.$$

The investigation of this new compound is not yet completed.

31. "The refractive power of certain organic compounds at different temperatures." By W. H. Perkin, Ph.D., F.R.S.

Having found that the magnetic relations of substances, when examined at temperatures wide apart, showed that certain variations took place after allowing for change of density, experiments having been made by the authors in reference to the refractive power of liquids under similar circumstances. After describing the apparatus used, results are given showing that the specific refractive energy

of the substances examined is not constant for all temperatures. The experiments were made at temperatures from about 14 to 92, and for the lines A, C, D, and F, the differences obtained were calculated for a variation of 100°, so that comparison could be more easily made, and are as follows:—

	$\frac{\mu_A - 1}{d}$.	$\frac{\mu_A - 1}{d}p$.
Aniline	0·00310	0·2897
Toluene	0·00329	0·2910
Heptane	0·00291	0·2914
Dimethylaniline.....	0·00253	0·3057
Phenyl iodide.....	0·00214	0·4378
Octyl iodide	0·00190	0·4549
Cinnamic ether.....	0·00324	0·7080
Methylene iodide.....	0·00401	0·8685

By comparing the lines A and F it was also found that the dispersion was slightly diminished by rise of temperature. When calculated by Lorentz's formula, the numbers gave higher results for high temperatures than for lower ones, showing the formula is not suitable for the calculation of experiments made at high temperatures. Ketteler's experiments with water, alcohol, and carbon disulphide are also referred to. The influence of heat, therefore, affects both the refractive power as well as the magnetic rotatory power of substances; the result, however, are not comparable as to the extent of change.

Discussion.

Dr. Gladstone remarked that in the original paper by Mr. Dale and himself, published in 1863, they had, as the result of an examination of 23 different liquids, come to the conclusion that $\frac{\mu - 1}{d}$ was "nearly a constant" at all temperatures. They had tested this for the theoretical limit of the spectrum according to Cauchy's formula, as well as for the lines A and H. Landolt and Wüllner seem to have expected that the slight differences recorded were due to experimental error, but on carefully repeating the experiments they arrived at a similar result. Dufet, in 1885, published an elaborate paper, in which he proved that the general law was not absolutely true, but a near approximation. Nasini and Bernheimer, in 1884, published very careful observations both on saturated and unsaturated compounds, dealing both with the specific refraction and dispersion; while Weegman and others have also contributed material to the general investigation of the subject.

Dr. Perkin's experiments were particularly valuable on account of

the indications they give that the rate of change of specific refraction is greater at high than at low temperatures, and as they afforded clearer proof than has been hitherto given that the specific dispersion does decrease with the temperature. If it should be found to be a general fact that the change is proportionally greater in saturated than in unsaturated compounds, and still greater in such bodies as cinnamic ether, another connection will have been established between this phenomenon and what we already know of refraction, dispersion and magnetic rotation.

The observation that the values decrease as the temperature rises if calculated by the old formula, while they increase as calculated from Lorentz's formula, seemed to be an argument in favour of the older formula; as the hotter liquid is approaching the condition of a gas, and it is well known that the refraction of a substance is somewhat smaller in the gaseous than in the liquid state.

Professor Thorpe said that it would be specially important to study the influence of temperature on refractive power in the case of liquids, such as acetic acid, which were believed to undergo molecular change; and it would also be interesting to know what was the behaviour of the phosphorus compounds, as the optical properties of many of these were most anomalous.

Mr. Hibbert thought that the superiority of the $\frac{\mu - 1}{d}$ formula over Lorentz's formula brought out by Dr. Perkin was an important result.

32. "Note on a volatile compound of iron and carbonic oxide." By Ludwig Mond, F.R.S., and F. Quincke, Ph. D.

The authors describe experiments from which they conclude that iron forms a volatile compound with carbonic oxide of the formula $Fe(CO)_4$, corresponding to that of nickel. Very finely divided iron —obtained by reducing iron oxalate by hydrogen at a temperature but little exceeding 400° and allowing it to cool to 80° in hydrogen— when heated in an atmosphere of carbonic oxide, gave a gas which burnt with a yellow flame; and on passing the gas through a heated tube a mirror of iron was formed at between 200° and 350°, while at higher temperatures black flakes of iron and carbon were deposited. Only about 2 grams of iron, however, was volatilised after six weeks treatment of 12 grams of the metal; it was necessary every five or six hours to interrupt the operation and to reheat the iron to 400° in hydrogen during about 20 minutes. When passing carbonic oxide at the rate of about $2\frac{1}{2}$ litres per hour, not more than 0·01 gram of iron was volatilised, corresponding to less than 2 c.c. of the compound $Fe(CO)_4$ in a litre of gas. The authors have effected an analysis of

the compound by passing the mixture of gases into mineral oil boiling between 250° and 300°, and heating the solution so obtained to 180°; iron free from carbon is then deposited and carbonic oxide gas is evolved. Five analyses are quoted, the results of which give a ratio of Fe : CO varying only from 1 : 4·03 to 1 : 4·264.

Discussion.

Dr. Armstrong said that the authors' discovery was even more interesting than that of the nickel compound which they had previously described in conjunction with Dr. Langer, on account of the explanation which it might be held to afford of the permeability of iron by carbonic oxide at high temperatures, as well as of the production of steel by the cementation process, phenomena to which Graham had drawn attention. Just as platinum was permeable by hydrogen and silver by oxygen at high temperatures, so iron was permeable by carbonic oxide: it might be supposed in each case, because a dissociable compound of the metal with the gas was formed.

Professor Thorpe, after referring to the value of authors' observation as shedding light on the production of steel by the cementation process, stated that in studying, in conjunction with Mr. Ellis, the interaction of nitrogen peroxide and carbonic oxide under the influence of finely divided platinum, he had recently had occasion to observe that platinum had the property of causing the separation of carbon from carbonic oxide.

Mr. Mond, in reply, said that, although the application of their discovery in the directions indicated had not escaped their notice, they had refrained from discussing such matters, as the compound was only obtained at low temperatures.

Dr. Armstrong said that this might well be the case; but, as Mr. Mond and Dr. Quincke had established the all-important fact that iron had a specific affinity for carbonic oxide, the argument he had used would apply, although the compound might not be sufficiently stable at high temperatures to exist alone.

33. "The formation of salts—a contribution to the theory of electrolysis, and of the nature of chemical change in the case of non-electrolytes." By Henry E. Armstrong.

The author draws attention to the recent researches of Claisen, W. Wislicenus and others, which clearly show that ethereal salts, such as ethylic acetate, form compounds with sodium ethylate, and to the bearing which these results have on the theory of the formation of salts generally. It may be supposed that in all cases the acid and the "base" in the first instance combine, and that the salt is formed

by subequent interactions within the molecule. In like manner, acids form dissociable compounds with water, and it is by the occurrence of change within such systems under the influence of an electromotive force that electrolysis is effected.

In those cases in which the compound is highly unstable and prone to dissociate, the opportunity for change to take place within the system is but slight, and consequently the acid is a weak one, and its solution of relatively low conducting power. In the case of non-electrolytes, the occurrence of change may, in like manner, be supposed to occur within complex systems formed by the union of the interacting substances—systems which are comparable with those formed by the union of acid and "base."

34. "Dibenzyl ketone." By Sydney Young. D.Sc., Professor of Chemistry, University College, Bristol.

Dibenzyl ketone was prepared by Popow (*Ber.*, **6**, 560) by the action of heat on calcium phenylacetate.

The author finds that when the calcium salt, dried at 130°, is heated in a hard glass tube in a combustion furnace, the yield is very poor, even when the temperature is kept as low as possible, and when a current of dry carbon dioxide is passed through the tube. After laborious purification of the product, not more than 27 per cent. of the theoretical amount of pure ketone was obtained.

The action of heat on the calcium salt was then more carefully studied, and it was found that the decomposition begins at about 360°, and is very rapid at 445°, the boiling point of sulphur.

A considerable quantity of calcium phenylacetate was then heated by means of the vapour of boiling sulphur in a special apparatus described fully in the paper. More than 50 per cent. of the theoretical was obtained by crystallisation of the crude product from small quantities of ether, and by fractionation and subsequent recrystallisation of the residues, the total yield of pure ketone was increased to 76·6 per cent.

Pure dibenzyl ketone melts at 33·0°, and boils at 330·55° under normal pressure.

35. "The vapour pressures of dibenzyl ketone." By Sydney Young, D.Sc., Professor of Chemistry, University College, Bristol.

Constant temperatures above 280°, the boiling point of bromonaphthalene, may be obtained by means of the vapour of mercury boiling under known pressure, but there are serious objections to this substance. Benzophenone gives very good results according to Crafts (*Amer. J. Sci.*, **5**, No. 5), but the boiling point, 306°,

is not sufficiently far removed from that of bromonaphthalene to give a good range of temperature. Dibenzyl ketone boils at 330·55°, and although it suffers a slight amount of decomposition on long continued boiling, the temperature of the vapour is not perceptibly affected. The ketone may also be readily purified by recrystallisation from small quantities of ether.

The vapour pressures from 230° to 280° were determined in a modified distillation bulb, the temperature being measured with a mercurial thermometer standardised by means of bromonaphthalene. At higher temperatures a mercury vapour pressure thermometer was employed, and the ketone was boiled in a wide glass tube, enlarged into a bulb at its lower end.

Four series of determinations were made with very concordant results.

The logarithms of the pressure were mapped against the temperature, and the constants for Biot's formula ($\log p = a \pm b\alpha^t$) were calculated from the values at 230°, 280° and 330°.

From these constants the vapour pressures were calculated at each 10° from 230° to 330°, and for each degree from 280° to 330°.

The results are tabulated in the paper.

36. "The vapour pressures of mercury." By Sydney Young, D.Sc., Professor of Chemistry, University College, Bristol.

In vol. **49**, pp. 37—50. of the Transactions, an account was given by Dr. Ramsay and the author of determinations of the vapour pressures of mercury at several widely different temperatures, and tables of vapour pressure, based on these results, were added. The highest temperature at which observations were made was that of the vapour of sulphur boiling under atmospheric pressure, and in calculating the results the boiling point of sulphur given by Regnault was taken as correct.

From a recent research by Callendar and Griffiths (*Phil. Trans.*, **182**, A. 119) it appears, however, that Regnault overestimated this temperature by nearly 4°, and the vapour pressures of mercury at high temperatures therefore require correction.

Messrs. Callendar and Griffiths have also redetermined the boiling point of mercury by means of their platinum thermometer, and the temperature they have observed is about 1·5° lower than that given in the tables of Ramsay and Young.

Two additional observations of the vapour pressures of mercury at 183·75° and 236·9° have been made, and from the previous results by Ramsay and Young (corrected at the highest temperature for the alteration in the boiling point of sulphur), the boiling point of

mercury given by Callendar and Griffiths, and the values at 183·75° and 236·9°, the vapour pressures of mercury at each 10° from 180° to 480°, and for each degree from 330° to 360° have been recalculated, and the tabulated results, with an account of the method of calculation, are given in the paper.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Coal and what we get from it, by R. Meldola. London 1891. From the Publishers.

Colour Measurement and Mixture, by W. de W. Abney. London 1891. From the Publishers.

Report of the Sixtieth Meeting of the British Association for the Advancement of Science, held at Leeds in September, 1890. London 1891. From the Association.

The Chemistry of Illuminating Gas, by N. H. Humphrys. London 1891. From the Author.

California State Mining Bureau: Tenth Annual Report of the State Mineralogist (W. Irelan, Jr.) for the year ending December 1, 1890. Sacramento 1890. From the Bureau.

II. *By Purchase.*

Handbuch der Elektrochemie und Metallurgie, von F. Vogel und A. Rössing. Stuttgart 1891.

A History of Chemistry from Earliest Times to the Present Day, by E. Meyer. Translated by G. McGowan. London 1891.

Les Virus, par S. Arloing. Paris 1891.

EXTRAORDINARY GENERAL MEETING.

June 25th, 1891. Professor Crum Brown, President, in the Chair.

The request of certain Fellows to the President to summon an Extraordinary General Meeting of the Society and the notice convening the meeting were read, and on the motion of the President it was agreed that the proposals submitted for amending and altering the bye-laws should be taken as read, printed copies having been circulated among the Fellows.

The President suggested that the most convenient course would be for the Fellows at whose request the meeting had been called to

explain and justify in general terms their proposals, and to leave the discussion of details to a later period. Mr. James Wilson, however, urged that, as specific resolutions had been submitted, the several bye-laws should be separately considered, and the President having agreed that this course would be in accordance with his ruling if the motion were confined in each case to an affirmation of the principle, Mr. Wilson moved: "That Bye-law I be altered in the sense indicated by the clauses already in the hands of the Fellows." He then indicated, with special reference to Clause 3, the reasons which, in the opinion of the memorialists, rendered such alterations desirable.

The motion was seconded by Dr. Teed.

Professor Tilden, in his capacity as President of the Institute of Chemistry, strongly deprecated the proposal that Fellowship of the Chemical Society should be regarded as a professional qualification.

Mr. Carteighe then moved the following amendment:—

> "That this meeting declines to pledge itself to any amendment or modification of the bye-laws which has not been approved and recommended to the Fellows for adoption by the Council."

Sir F. A. Abel seconded the amendment.

Mr. Cassal, Mr. Lloyd and Dr. Newton addressed the meeting in support of the original motion. Mr. Warington, Mr. Page, Dr. Odling and Mr. Friswell spoke in favour of the amendment.

Mr. Clayton spoke in answer to objections made by Mr. Page to the use of the letters F.C.S., &c., under certain circumstances.

Mr. Goffin also spoke.

Mr. Lloyd and Dr. Teed having been nominated tellers for the original motion, and Messrs. Groves and Warington for the amendment, the meeting then divided.

The votes recorded were—

For the amendment.....	137
Against „	47
Majority for the amendment	90

Professor Odling then took the Chair, and declared the following resolution carried:—

> "That this meeting declines to pledge itself to any amendment or modification of the bye-laws which has not been approved and recommended to the Fellows for adoption by the Council."

On the proposal of Dr. Teed, seconded by Mr. Carteighe, a vote of thanks to the President for his conduct in the Chair was carried.

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Issued 17/11/1891.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 101. Session 1891-92.

Titles of Papers communicated to the Society and printed in the Transactions during the recess.

37. "Researches on the terpenes. On camphene." By J. E. Marsh, M.A., and J. A. Gardner.

38. "Action of nitrosyl chloride on metals." By J. J. Sudborough, B.Sc.

39. "The influence of temperature on germinating barley." By T. Cuthbert Day.

40. "Researches in the triazine series." By Raphael Meldola, F.R.S., and Martin O. Forster.

41. "The action of picric chloride on amines in presence of alkali." By G. S. Turpin, M.A., D.Sc.

42. "Researches on the terpenes. II. On turpentine." By J. E. Marsh, M.A., and J. A. Gardner.

43. "On diphenylisosuccinic acid and β-diphenylpropionic acid." By G. G. Henderson, D.Sc., M.A.

44. "Preparation and properties of ethyl hydrogen fumarate and ethyl hydrogen maleate." By John Shields, Ph.D., B.Sc.

45. Action of ammonia on ethereal salts of organic acids." By S. Ruhemann, Ph.D., M.A, and R. S. Morrell, B.A.

46. "Contributions to the knowledge of mucic acid." By S. Ruhemann, Ph.D., M.A., and S. F. Dufton, B.A., B.Sc.

47. "Orthoquinolinehydrazine." By S. F. Dufton, B.A., B.Sc.

48. "Oxidation of cobalt salts by electrolysis." By Hugh Marshall, D.Sc.

49. "The persulphates." By Hugh Marshall, D.Sc.

50. "Acetylcarbinol." By W. H. Perkin, Jun., Ph.D., F.R.S.

51. "Action of methylene iodide on the disodium compound of ethyl pentanetetracarboxylate. Synthesis of hexamethylene derivatives." By W. H. Perkin, Jun., Ph.D., F.R.S.

52. "Synthesis of homologues of pentanetetracarboxylic acid and of pimelic acid." By W. H. Perkin, Jun., Ph.D., F.R.S., and Bertram Prentice.

53. "The synthetical formation of closed carbon chains. Part I (*continued*). The action of ethylene bromide on the sodium compounds of ethyl acetoacetate and ethyl benzoylacetate. By T. Rhymer Marshall, D.Sc., and W. H. Perkin, Jun., Ph.D., F.R.S.

54. "On the vapour pressures and molecular volumes of acetic acid." By Sydney Young, D.Sc.

55. On the vapour pressures and molecular volumes of carbon tetrachloride and stannic chloride." By Sydney Young, D.Sc.

56. "On the freezing points of triple alloys of gold, cadmium, and tin." By C. T. Heycock, M.A., and F. H. Neville, M.A.

57. "The sulphonic derivatives of camphor." By J. E. Marsh, M.A., and H. H. Cousins, B.A.

58. "Eulyte and dyslyte." (A correction.) By Henry Bassett.

November 5th, 1891. Mr. W. Crookes, F.R.S., Vice-President, in the Chair.

Mr. J. Tudor Cundall was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. George James Allen, Ivy House, Bolton Road, Pendleton; George Alfred Ashcroft, 88, Alexandra Road, Manchester; Harold Alger, The Manor House, Stoke, Devonport; Edward Charles C. Baly, Bank

of England; Thomas William Berry, Shireoaks, Worksop, Notts; Samuel Francis Burford, Eastleigh, Queen's Road, Leicester; John Bairstow, 32, Sealand Road, Chester; J. Treeby Barratt, Mostyn, North Wales; John Redman Bovell, Dodds, Barbados; John C. Chorley, Lodge Lane, Bewsey, Warrington; George Edward Cory, The Public School, Grahamstown, South Africa; Thomas Darling, 1, Palace Street E., Berwick-on-Tweed; Charles E. Eastick, Myrtle Bank, Leyton; Percy Elford, Christ Church, Oxford; Lionel William Fulcher, 37, Melford Road, Lordship Lane, S.E.; George German, jun., Ashby-de-la-Zouch; Alfred Daniel Hall, Martyn Road, Guildford; Archibald Hall, 34, Bishopsgate Street; John Holliday, 7, Aglionby Street, Carlisle; John Walter Leather, 15, Bradgate Road, Catford, S.E.; Lionel Ludlow, 90, Walter Road, Swansea; John Willis Marshall, 10, Palatine Square, Burnley; Daniel McLaren, B.Sc., 30, Raleigh Street, Nottingham; Joseph Morris, Stamford Street, Mossley, near Manchester; William Naylor, 182, Newhampton Road, Wolverhampton; Thomas Neilson, 26, Harrington Road, Workington, Cumberland; Abhayacharan Sanyal, M.A., Muir Central College, Allahabad; Walter Thorp, 3, Melbourne Villas, Headingley, Leeds; A. W. Winterton, 6, Lindum Terrace, Rotherham; John Henry Wilson, 29, Radford Street, Coventry.

The following papers were read:—

59. "The magnetic rotatory power of solutions of ammonium and sodium salts of some of the fatty acids." By W. H. Perkin, Ph.D., F.R.S.

Ostwald, in his paper on magnetic rotation (*C.S. Trans.*, 1891, 198), has argued that the peculiar results obtained by the author in the case of solutions of acids and of ammonium salts, &c., are in accordance with the electrolytic dissociation hypothesis; and has suggested that since salts formed from weak acids are as good conductors as those formed from strong ones, we may expect in this case, also, marked deviations from the calculated values. The same chemist, in his work on Solutions, considers that there can be no doubt that such salts as ammonium formate, &c., when in aqueous solution, would show molecular rotations which would not be the sums of the rotations of the components of the salts, as must (nearly) be the case if the view put forward by the author be correct, that such salts are almost entirely dissociated into acid and base. Experiments made with the object of throwing further light on the subject have afforded the following results:—

	Mols. water to 1 mol. salt.	Mol. rot.	Average mol. rot.
Ammonium formate	3·00	3·363	
,, ,, ...	8·78	3·394	
,, ,, ...	10·00	3·333	3·363
,, acetate	4·75	4·246	
,, ,, ...	13·13	4·247	4·246
,, propionate	2·86	5·255	
,, ,, ...	10·26	5·263	5·259
Sodium formate	5·40	2·364	
,, ,, ...	12·54	2·331	2·347
,, acetate	11·23	3·281	3·281
,, propionate	7·00	4·308	4·308
,, butyrate	6·81	5·332	5·332

It will be seen that the rotatory powers of the ammonium salts do not vary with dilution; there can be little doubt that this is true also of the sodium salts, as sodium formate shows no difference on dilution. Comparing the experimental values obtained in the case of the ammonium salts with those afforded by the constituent acid and ammonia, the following results are obtained:—

CH_2O_2	1·671	$C_2H_4O_2$	2·525	$C_3H_6O_2$	3·462
NH_3	1·818		1·818		1·818
	3·489		4·343		5·280
Am. salt ..	3·363		4·246		5·259
Diff...	0·126		0·095		0·021

As might be expected, as reduction of rotatory power always attends combination, the values are slightly less in the case of the salts. The author points out that the reduction is very nearly the same as that which takes place in the formation of the corresponding ethereal salts, and as these latter salts are anhydrous, the results may be held to justify the conclusion that the values obtained for ammonium salts in solution are practically those of the dry salts, and, therefore, that Ostwald's views are inapplicable. In the case of sodium salts, it is more difficult to arrive at a conclusion, as the value of sodium is unknown, but it is shown that whatever influence water has on them, it is to be supposed that it acts to the same extent on all the four salts examined.

60. "Note on the action of water gas on iron." By Sir H. E. Roscoe and Frank Scudder.

During some experiments which the authors have recently been

making on the application of water gas for illuminating purposes by means of the well-known Fahnehjelm system, it was occasionally observed that after the water gas had impinged on the comb for some hours a deposition of ferric oxide was formed on the magnesia rods, the result being that the illuminating power was considerably lowered.

It was at first suggested that the iron came from the particles of dust which were present in the atmosphere of the steel works where these experiments were being conducted. Further examination of the tips of the steatite burners showed, however, that the deposit of ferric oxide was "coralloid" and that, therefore, it could not be produced from dust in the atmosphere but was contained in the gas itself. In order to ascertain whether the iron was in a gaseous state or in the form of finely divided particles, the gas was filtered through several tight plugs of cotton wool; but as a similar deposit was observed after four or five hours it was concluded that the water gas contained a volatile iron compound.

These facts, although interesting, only showed that the quantity of the volatile iron compound was extremely small, apparently precluding all hope of extracting sufficient of the material for analysis. Nevertheless the occurrence of iron, even in these minute quantities, was a most serious bar to the technical application of water gas as an illuminant, and the question of its origin as well as its removal became of practical interest.

In the course of experiments made for another purpose, water gas was compressed in steel cylinders to a pressure of 8 atmospheres, and on burning the gas immediately after compression no visible alteration in the colour of the flame or in the amount of iron contained in the gas was observable; but after the compressed gas had remained in the cylinders for about a month, it was found that when it was burned from a steatite burner the flame was highly luminous and instantly deposited on the Fahnehjelm comb a yellowish-red coating of ferric oxide: proving that a much larger quantity of iron was contained in the gas which had been kept than in the original compressed gas.

On passing a small quantity of the gas through a piece of combustion tubing heated externally by a Bunsen burner, a large deep-black mirror was rapidly formed, which proved on analysis to be metallic iron, free from carbon, arsenic and antimony.

The flame, however, still remained strongly luminous, particles of metallic iron burning brightly in it, whilst either a black mirror of metal or one of ferric oxide was deposited on a porcelain plate held above it according to the position in which the plate was held. On inserting a plug of cotton wool between the heated portion of the tube

and the burner, the flame instantly became non-luminous, and in a few seconds the cotton wool nearest to the heated part of the tube became black; in a short time the whole plug was deeply stained with finely divided metal. Hence it was evident that under a pressure of 8 atmospheres the carbonic oxide contained in water gas (about 39 per cent. of its bulk) slowly attacked metallic iron at the ordinary atmospheric temperature.

In a preliminary determination in which about 30 litres of gas was burned in half an hour, the weight of the metallic iron deposited as a mirror amounted to 0·0322 gram, whilst that found on the plug of cotton wool was 0·0406 gram, a total of 0·0728 gram of iron, equal to 2·4 milligrams per litre.

Although the compound, which is, doubtless, the iron carbonyl of Mond and Quincke, is only present in this small quantity, the authors have found that it can readily be liquefied if the gas be passed through a cotton-plugged tube and then led into a U-tube surrounded by a mixture of salt and ice: a few drops of turbid liquid thus deposited became clear on treatment with a little hydrochloric acid, and on adding potassium ferrocyanide a deep blue colour was obtained.

The authors hope, before long, to communicate more detailed information as to the causes of the occasional occurrence of the volatile iron compound in water gas and as to its nature. The action of water gas on other metals will also receive their attention.

Discussion.

The Chairman referred to the fact that at the recent British Association meeting at Cardiff Mr. Mond had exhibited specimens not only of liquid iron carbonyl but also of a solid compound of iron with carbonic oxide.

Professor Ramsay stated that he had found that the compound of nickel with carbonic oxide was formed in the cold, the action frequently going on for days. He subsequently added, in reply to a question by Mr. Groves whether dry pure carbonic oxide acted on iron, that in the case of nickel, the gas acted equally well when dried by phosphoric anhydride.

Sir Henry Roscoe, in the course of his account, had mentioned that ordinary coal gas contained traces of iron, pointing out that this was the cause of the stain observed on steatite burners. Referring to this point, Dr. Thorne mentioned that he had recently had occasion to detect iron in compressed coal gas, which was now frequently used for the production of the limelight. In using such gas, it was sometimes noticed that the lime cylinder acquired a brown deposit, and

it was owing to this circumstance that he was led to examine the gas.

61. "The dissociation of liquid nitrogen peroxide." By J. Tudor Cundall, B.Sc., Lecturer on Chemistry in the Edinburgh Academy.

The author has determined, by colorimetric methods, the relative amount of NO_2 formed in liquid nitrogen peroxide (i) by dilution with chloroform, (ii) by rise of temperature. He has also ascertained the absolute amount of dioxide by comparing the colour of the liquid solution with that of the gas containing a known amount of nitrogen dioxide. The results go to show that, on dilution, (i) dissociation takes place very slowly at first, but more rapidly when less that 5 per cent. of the peroxide is taken; (ii) that solutions of the peroxide dissociate more rapidly than the pure liquid on rise of temperature. In the most dissociated solution yet examined, viz., one to which had been added 1·44 per cent. of peroxide by vol. at 25° C., not more than 1·22 per cent. of NO_2 was present.

Discussion.

Professor Ramsay pointed out that the fact established by Mr. Cundall, that nitrogen peroxide was dissociated to but a slight extent on dilution unless the solution were very dilute, was a confirmation of the result which he had obtained on determining the molecular weight of the peroxide by Raoult's method.

Professor Thorpe suggested that the rate of dissociation might possibly be ascertained by determining the relative densities of solutions of nitrogen peroxide at different temperatures.

Mr. Cundall thought that the variation was too slight to permit of the application of such a method.

62. "Ortho- and para-nitro-orthotoluidine." By Arthur G. Green and Thos. A. Lawson, Ph.D.

It has been shown by Nölting and Collin (*Ber.*, 1884, 265) that when orthotoluidine sulphate is nitrated at a low temperature in presence of a large excess of sulphuric acid, *para*nitro-orthotoluidine, $C_6H_3Me(NH_2)(NO_2)$ [1 : 2 : 4], results. This isomer appears to have been considered to be the only product of the interaction under these conditions, but the authors have found that this is by no means the case, for besides the paranitro-orthotoluidine (about 75 per cent.) there is formed about 3 or 4 per cent. of *meta*nitro-orthotoluidine, $C_6H_3Me(NH_2)(NO_2)$ [1 : 2 : 5], and about 20 per cent. of *ortho*nitro-orthotoluidine, $C_6H_3Me(NH_2)(NO_2)$ [1 : 2 : 6]. The latter,

	CH_3 NH_2 NO_2.	CH_3 OH NO_2.	CH_3 NH_2 NH_2	CH_3 NHAc NHAc	CH_3 NH_2 N_2O	CH_3 NHAc N_2O	CH_3 NH_2 N_2	CH_3 NHAc N_2	CH_3 Cl NO_2	CO_2H Cl NO_2
1 : 2 : 4	M. p. 107° (Nölting and Collin), 107·5°, very sharp (G. and L.). Orange prisms; very sweet taste.	M. p. 107—108° (Nölting and Collin). Fine, yellowish needles; very sweet taste.	M. p. 99°. Prismatic crystals.	M. p. 221° (Tiemann), 224° (Laderburg). Does not sublime in flocks.	M. p. 168° (Limpricht) (G. and L.). Yellow needles or orange prisms.	M. p. 290° (G. and L.). Small, white needles.	M. p. 197° (Limpricht), 203° (G. and L.). Orange, prismatic needles.	M. p. 306° (G. and L.). Small, yellow needles.	M. p. 65·5° (Wachendorff), 68° (G. and L.). Long, white needles.	M. p. 136—137° (Wachendorff).
1 : 2 : 6	M. p. 91·5° (Bernthsen) (G. and L.). Fine, light-yellow needles; not sweet.	M. p. 142—143° (Uhlmann), 143—144° (G. and L.). Compact, yellow needles; slightly sweet.	M. p. 103·5° (Uhlmann), 105° (G. and L.). Prisms.	M. p. 202—203° (G. and L.). Sublimes in very light flocks.	M. p. 149° (G. and L.). Pale-yellow plates.	M. p. 307° (G. and L.). Small, white, flat needles.	M. p. 175° (G. and L.). Orange plates.	M. p. above 340° (G. and L.). Small, yellow needles.	M. p. 37° (G. and L.). Long, white needles.	M. p. 161° (G. and L.). White, prismatic needles.

which up to the present has only been obtained by reduction of the consecutive dinitrotoluene, like paranitro-orthotoluidine, has the NH_2 and NO_2 groups relatively in the meta-position, and hence the simultaneous formation of these two isomers (the 1 : 2 : 6 and the 1 : 2 : 4) by nitration of orthotoluidine in presence of sulphuric acid might have been theoretically expected.

The separation of the orthonitro-orthotoluidine from the mixture is effected by taking advantage of the greater solubility of this isomer in slightly warm water.

Having at their disposal considerable quantities of the ortho- and para-nitro-orthotoluidine, the authors have made a comparison of these two isomers and of their products of reduction and other derivatives, which is summarised in the table (p. 130).

63. "Researches on the gums of the arabin group. Part II. Geddic acids. Gedda gums; the dextrorotatory varieties." By C O'Sullivan.

The Gedda gums described consist of the calcium, magnesium and potassium salts of gum acids, the calcium salt predominating, together with more or less nitrogenous matter, which is probably in some way combined with a true gum acid.

They dissolve easily in water, forming a yellow or reddish syrup, neutral to test-paper, which is dextrorotatory.

If the solution be acidified and dialysed for some time, the whole of the ash may be separated, and if alcohol be added carefully to the dialysed liquid, a powdery precipitate first separates, which contains the whole of the nitrogenous bodies and some gum acid; on allowing the precipitate to deposit, and then decanting the clear, supernatant liquid and adding alcohol, a syrupy precipitate is obtained, consisting of a mixture of the gum acids present in the natural gum. By repeatedly fractionating the aqueous solution of these gum acids by alcohol, they were separated from one another and obtained in a pure state.

The gum acids contained in any one sample of gum bear a very simple relation to one another, and they are also intimately related to the gum acids contained in other samples. These relationships are indicated in the table (p. 132).

Of these gum acids, those having the highest molecular weight are most soluble in dilute alcohol.

The gum acid of gum arabic is similarly constituted, being, in fact, diarabinantetragalactanarabic acid, $2C_{10}H_{16}O_8.4C_{12}H_{20}O_{10}.C_{23}H_{30}O_{18}$; and the acids present in the third sample of Gedda gum described are similarly constituted, geddic and arabic acids being isomeric.

Name.	Formula.	$[\alpha]_D$.	Per cent. BaO in Ba salt.
Gedda gum I.			
Tetr-arabinan-tri-galactan-geddic acid	$4C_{10}H_{16}O_8 \cdot 3C_{12}H_{20}O_{10} \cdot C_{23}H_{32}O_{19}$	+59°	5·59
Tri-arabinan-tri-galactan-geddic acid	$3C_{10}H_{16}O_8 \cdot 3C_{12}H_{20}O_{10} \cdot C_{23}H_{32}O_{19}$	+49°	6·05
Di-arabinan-tri-galactan-geddic acid	$2C_{10}H_{16}O_8 \cdot 3C_{12}H_{20}O_{10} \cdot C_{23}H_{32}O_{19}$	+43°	6·75
Mon-arabinan-tri-galactan-geddic acid	$C_{10}H_{16}O_8 \cdot 3C_{12}H_{20}O_{10} \cdot C_{23}H_{32}O_{19}$	+37°	7·65
Gedda gum II.			
Non-arabinan-tetra-galactan-geddic acid	$9C_{10}H_{16}O_8 \cdot 4C_{12}H_{20}O_{10} \cdot C_{23}H_{30}O_{18}$	+110°	3·46
Hept-arabinan-tetra-galactan-geddic acid	$7C_{10}H_{16}O_8 \cdot 4C_{12}H_{20}O_{10} \cdot C_{23}H_{30}O_{18}$	+100	3·93
Pent-arabinan-tetra-galactan-geddic acid	$5C_{10}H_{16}O_8 \cdot 4C_{12}H_{20}O_{10} \cdot C_{23}H_{30}O_{18}$	+90°	4·55
Tri-arabinan-tetra-galactan-geddic acid	$3C_{10}H_{16}O_8 \cdot 4C_{12}H_{20}O_{10} \cdot C_{23}H_{30}O_{18}$	+80°	5·40

The composition and partial constitution of any one of the gum acids which have been as yet examined may be expressed by the general formula $C_{23}H_{38-2n}O_{22-n} \cdot nC_{12}H_{20}O_{10} \cdot pC_{10}H_{16}O_8$.

When a solution containing 2 per cent. H_2SO_4 of any one of these gum acids is heated at 80—100° C. for 10—30 minutes, the gum acid is hydrolysed, yielding arabinon and a gum acid of lower molecular weight, the whole of the arabinon residue indicated in the general formula being liberated. The change may be expressed as follows:—

$$C_{23}H_{38-2n}O_{22-n} \cdot nC_{12}H_{20}O_{10} \cdot pC_{10}H_{16}O_8 + pH_2O = C_{23}H_{38-2n}O_{22-n} \cdot nC_{12}H_{20}O_{10} + pC_{10}H_{18}O_9.$$

The greater portion of the arabinon thus produced is hydrolysed to arabinose, $C_{10}H_{18}O_9 + H_2O = 2C_5H_{10}O_5$.

It is possible by carefully restraining the hydrolytic action to obtain gum acids which still contain the arabinon residue, but, under the conditions given, practically the whole of the arabinose obtainable is produced.

The gum acids thus produced are separated from the sugars by treatment with alcohol; they very closely resemble the gum acids existing in the natural gums, but are less optically active, and less soluble in weak alcohol.

As is evident from the formulæ given above, any one of the gum acids contained in a given sample of gum, when thus hydrolysed, yields the same gum acid; and the acids obtained from the natural

acids of different samples are closely related together. This is indicated in the following table :—

Obtained by the action of sulphuric acid on the gum acids contained in—	Name.	Formula.	$[\alpha]_D$.	Per cent. BaO in Ba salt.
Gedda gum III.....	Penta-galactan-geddic acid..	$C_{23}H_{38}O_{17}\cdot 5C_{12}H_{20}O_{10}$	+30°	6·51
Gedda gum II	Tetra-galactan-geddic acid..	$C_{23}H_{30}O_{18}\cdot 4C_{12}H_{20}O_{10}$	+22°	7·49
Gum arabic Gedda gum I.....	Tri-galactan-geddic acid..	$C_{23}H_{32}O_{19}\cdot 3C_{12}H_{20}O_{10}$	+20°	8·81

It is noteworthy that these acids bear a relation to one another similar to that of the different acids contained in any one sample of the natural gums. The most marked point of difference between these gum acids and those present in the natural gum is their behaviour when heated with a 2 per cent. solution of sulphuric acid; they offer great resistance to the hydrolytic action of this acid, but are slowly broken down by several hours' digestion, the galactan residue being removed, and acids of successively lower weight being formed; the lowest stage is represented by the general equation

$$C_{23}H_{38-2n}O_{22-n}\cdot nC_{12}H_{20}O_{10} + 3nH_2O = C_{23}H_{38}O_{22} + 2nC_6H_{12}O_6.$$

The properties of the compound $C_{23}H_{38}O_{22}$ have not yet been very accurately determined, the difficulty being to obtain a sufficient quantity.

This gum acid and the others obtained after the partial hydrolysis of the galactan residue can only be precipitated from their concentrated aqueous solutions by very strong alcohol; they are dialysable, and strongly acid.

Those obtained from Gedda gum are highly dextrorotatory, whilst those from gum arabic, although otherwise identical, are inactive.

64. "Some compounds of the oxides of silver and lead." By Emily Aston, B.Sc.

The author finds that on following the directions given by Wöhler (*Pogg. Ann.*, 1837, **41**, 344) for the preparation of the compound $Ag_2O,2PbO$, the product varies in composition, the highest percentage of silver obtainable being 49·01, whereas the amount required for Wöhler's compound is 34·23.

When a mixture of lead and silver hydroxides is allowed to stand in presence of caustic soda, a change of colour occurs, and after repeated extraction with caustic soda, a substance is left having a composition nearly that required by the formula $2Ag_2O,PbO$. A product of similar composition is obtained by precipitating the mixed nitrates of lead and silver, and exhaustively extracting with caustic soda.

Attempts to prepare compounds of lead oxide with the oxides of barium, strontium, sodium and potassium were unsuccessful.

65. "The electrolysis of potassium acetate solutions." By T. S. Murray, D.Sc.

On electrolysing a very dilute aqueous solution of potassium acetate, only hydrogen and oxygen are evolved; if the solution be a concentrated one, the gaseous product is a mixture of ethane, hydrogen, oxygen, methyl acetate (trace) and carbon dioxide: a portion of the carbon dioxide arises from oxidation of some part of the electrolyte, or product of the electrolysis.

The author has investigated the influence of concentration of solution, strength of current, size of electrodes, temperature, &c., on the course of the electrolysis. He proves the absence from the gas of acetone, methyl oxide, ethylene or any unsaturated hydrocarbon.

On diluting the solution of acetate, the amount of ethane produced decreases, at first very slowly, but finally with great rapidity. For instance,

A 60	per cent.	solution	gave ethane	= 80·0 (hydrogen = 100).
,, 11·77	,,	,,	,,	= 73·5
,, 1·84	,,	,,	,,	= 50·8
,, 0·50	,,	,,	,,	= 0·003

Reducing the current has a similar influence. With rise of temperature, the ethane diminishes in quantity, more rapidly the higher the temperature, and ceases to be formed at about 100° C.

In contradiction to Jahn, he finds that the employment of a large anode reduces the yield of ethane, the largest yield being obtained by the use of a very small anode; variations in the cathode do not influence the electrolysis. The presence of acetic acid, or of alkali, even in small quantity, reduces the yield of ethane.

The oxidation of the electrolyte to carbon dioxide, which proceeds simultaneously with the formation of ethane, is affected very differently by changes in the several conditions. Thus for a given yield of ethane = 25 say (hydrogen = 100), the corresponding oxidations produced are by change of current, 96; by varying size of anode, 68;

by varying concentration, 60; by varying the temperature, 50; possible oxidation being taken as 100. With a yield of ethane about 75, no matter how it is obtained, the oxidation is always about the same, namely, 94.

The results of the investigation are illustrated by a series of curves. The author believes that he has demonstrated that the ethane is formed, not by a partial oxidation of acetic acid, as Bourgoin, Jahn and Bunge believe, but that it results from a simple interaction of the acetions ($CH_3 \cdot COO$). He finds that the yields of ethane obtained from equivalent solutions of potassium, sodium and calcium acetates are equal.

66. "A new method of preparing β-dinaphthylene oxide and the constitution of its tetrasulphonic acid." By W. R. Hodgkinson and L. Limpach.

The method in question is to heat the sodium salt of 2 : 3′-β-naphtholsulphonic acid (Schaefer's acid) to low redness; the distillate also contains β-naphthol and β-dinaphthyl ether: the former having been extracted by alkali, the residue is dissolved in acetic acid; as the solution cools, the oxide separates as a yellow, fluorescent substance, and when recrystallised forms rhombic plates melting at 153°. Its picrate crystallises from alcohol in dark-red needles melting at 134°. It is easily converted into a tetrasulphonic acid.

The same tetrasulphonic acid is formed by the continued action of sulphuric acid on β-naphthol.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Collected Papers on Allotropic Silver, by M. Carey Lea. With Atlas of Specimens. 1891. From the Author.

Undersökningar inom Piazinserien, af P. W. Abenius. Upsala 1891. From the Author.

Die Entwickelung der Elemente. Entwurf zu einer biogenetischen Grundlage für Chemie und Physik, von G. Wendt. Berlin 1891. From the Author.

Supplement to the Companion to the latest edition of the British Pharmacopœia, including the additions of 1890, by P. W. Squire and A. H. Squire. London 1891. From the Authors.

Smithsonian Institution. Annual Reports of Ethnology, by J. W. Powell. Fifth Annual Report, 1883–84. Washington 1887. Sixth Annual Report, 1884–85. Washington 1888.

From the Institution.

An Introduction to the Science and Practice of Photography, by Chapman Jones. 2nd Edition. London 1891.

From the Author.

The Chemistry of the Farm, by R. Warington. 6th Edition. London 1891. From the Author.

Examination of Water for Sanitary and Technical Purposes, by H. Leffmann and W. Beam. 2nd Edition. London 1891.

From the Publishers.

Short Treatise on Building Materials, by J. Scorgie. 2nd Edition. Aberdeen 1891. From the Author.

Piesse's Art of Perfumery. 5th Edition. Edited by C. H. Piesse London 1891. From the Editor.

A Textbook of the Science of Brewing, by E. R. Moritz and G. H. Morris. London 1891. From the Authors.

Geological and Natural History Survey of Canada. Annual Report (New Series), Vol. IV, 1888–89. Montreal 1890.

From the Survey.

Pamphlets presented by the Authors.

Theoretic Rationale of an improved design of an Open-Hearth Furnace, by B. H. Thwaite. Brierly Hill 1891.

The Variation of the Magnetic Needle at Paris, by G. T. Carruthers. 1891.

Thiacetessigester, von C. T. Sprague. Gottingen 1890.

Glacier Observations, by Marshall Hall. (From the Alpine Journal.) 1891.

The Proteids or Albuminoids of the Oat-kernel, by T. B. Osborne. 1890.

Mill Engines, by H. B. Thwaite. Leeds 1891.

Volumes moléculaires des combinaisons $C_pH_qO_r$, à leur points d'ébullition, par J. A. Groshans. Paris 1891.

Reports of the results obtained on the Experimental Fields at Dodd's Reformatory, by J. B. Bovell. Bridgetown 1890.

Food Preservation and Food Preservatives, by C. A. Crampton. Washington 1881.

Influence of Food, Animal Idiosyncrasy and Breed on the Composition of Butter, by H. W. Wiley. Toronto 1889.

Composition of Sorghum Seed with reference to its Feeding Value, by H. W. Wiley. Toronto 1889.

Onderzoek naar de Plantenstoffen von Nederlandsch-Indie, door M. Greshoff. Batavia 1890.

Discours prononcés aux Funerailles de M. Eugène Peligot, le 18 Avril, 1890.

Ueber Feuerbestattung, von F. Goppelsroeder. Mülhausen 1890.

Considerations on the subject of Solar Heat, by P. W. Boulton. London 1890.

I. The Analysis of Cupric Bromide and the Atomic Weight of Copper; II. Cupric Oxybromide, by T. W. Richards. 1890.

Hops and Bitter Principles, by C. E. Sohn. London 1890.

Etudio sobre plata allotropica obtenida por reduction con el Malato ferroso, por C. F. de Landero. Mexico 1890.

Beziehungen zwischen Absorption und Empfindlichkeit sensibilisirten Platten, von J. J. Acworth. Leipzig 1890.

Interstellar Æther, by A. S. Merry. London 1891.

II. *By Purchase.*

Die Chemie des Pyridins und seine Derivate, von A. Calm und K. v. Buchka. 2te Lieferung. Braunschweig 1891.

An Introduction to the Study of Metallurgy, by W. C. Roberts-Austen. London 1891.

At the next meeting, on Thursday, November 19th, a lecture will be delivered on "Colour Photometry," by Captain Abney, C.B., F.R.S.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE NEXT BALLOT.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

Alger, Harold,

The Manor House, Stoke, Devonport.

Manufacturing Chemist (Messrs. Burnard and Alger, Limited, Plymouth Chemical Works). Has studied Chemistry at the Royal College of Science, South Kensington, for three years.

T. E. Thorpe. W. P. Wynne. A. K. Miller.
Alfred E. Tutton. Chapman Jones. William Tate.

Ashcroft, George Alfred,

88, Alexandra Road, Manchester.

Analytical Chemist. Four years student in the Owens College. Obtained the College Certificate in Applied Chemistry on the completion of four years' study in Chemistry, Physics, and Mathematics; two years in Dr. Burghardt's Analytical Laboratory.

Harold B. Dixon. G. H. Bailey. Arthur Harden.
R. Ormandy. C. Schorlemmer.

Allen, George James,

Ivy House, Bolton Road, Pendleton.

Assistant to Dr. Burghardt, Dalton Laboratory. Two years student in Chemical Laboratories, Owens College; one year in the University Laboratory of Tübingen.

Harold B. Dixon. Julius B. Cohen. G. H. Bailey.
C. Schorlemmer. G. J. Fowler.

Baly, Edward Charles Cyril,

Bank of England.

Studied Chemistry for four years at University College, London.

William Ramsay. John Norman Collie. R. T. Plimpton.
Watson Smith. C. F. Baker.

Berry, Thomas William,

Shireoaks, Worksop, Notts.

Schoolmaster (Certif. 1st Div.) and (Certif. 1st Class) Science Teacher. Student in St. John's College (Laboratory), London, S.W., two years; obtained 2nd Prize in Chemistry; 1st Class Teacher's Certificate in Theoretical Chemistry; 1st Class Teacher's Certificate Practical Chemistry, South Kensington Science Department; Advanced Certificate in Physics (Electricity, Sound, Light, and Heat); Agriculture (Chem.), Physiology, Physiography, Hygiene, &c., and Science Lecturer at the Mechanics' Institute.

Wm. B. Hards, B.A. — Duncan T. Richards.
James Taylor, B.Sc., &c. — *Alexander Esilman.*
Wilfred Irwin. — *A. G. Perkin.*
R. L. Taylor.

Burford, Samuel Francis,

Eastleigh, Queen's Road, Leicester.

Analytical Chemist and Pharmacist. Late Teacher of Practical Chemistry to the Leicester and Leicestershire Chemists' Association. Studied Chemistry at the South London School of Pharmacy. Medallist in Advanced Chemistry. Passed the Major Examination of the Pharmaceutical Society, and afterwards studied Analytical Chemistry for two years under Dr. Muter.

Chas. Turner. — Jno. Geo. Frederick Richardson.
W. Henry Dodd. — Leonard de Koningh.
H. N. B. Richardson. — Lewis Ough.
E. Norman Langham. — *M. Carteighe.*

Bairstow, John,

32, Sealand Road, Chester.

Manager of Chemical Works.

W. F. Lowe. H. Broadbent. S. Watmough Webster.
J. Carter Bell. *Percy C. Bell.*

Barratt, J. Treeby,

Mostyn, North Wales.

Analytical Chemist. Studied Theoretical and Practical Chemistry privately and at Harris' Institute, Preston, where I passed in Advanced Practical Chemistry. Four years Assistant Chemist with the Darwen and Mostyn Iron Company, Limited, and for the last three years Head Chemist at the Talladega Iron and Steel Company, Talladega, U.S.A. Special experience in the analysis of Ferro-manganese, Ferro-chrome, &c., and materials used in their manufacture.

Frank B. Last. Richard Dormer. Saml. Sutcliffe.
John Pattinson. *Edwd. Riley.*

Bovell, John Redman,

Dodds, Barbados.

Superintendent of the Botanical and Experimental Station at Dodds Reformatory. Engaged on researches to ascertain the Manurial requirements of the Sugar Cane.

J. B. Harrison, William Douglas.
George Carrington, F.H.A.S. Francis Watts.
E. E. H. Thorne.

Chorley, John C.,

Lodge Lane, Bewsey, Warrington.

Chemical student for two years at Owens College, Manchester. Chemical student for two years at University College, London.

William Ramsay. R. T. Plimpton.
John Norman Collie. Watson Smith. C. F. Baker.

Calder, William A. S.,

45, Barrington Road, Brixton, S.W.

Student (Chemistry), Royal College of Science, South Kensington. Two years in Chemical Laboratory, Royal College of Science, London.

T. E. Thorpe. W. P. Wynne. A. E. Tutton.
William Tate. A. K. Miller. *Chapman Jones.*

Cory, George Edward,

The Public School, Grahamstown, South Africa, also King's College, Cambridge.

Vice-Principal of above. B.A. Natural Science Honours, Cambridge. Three years Demonstrator of Chemistry in the University Laboratory at Cambridge. Now Lecturer on Chemistry in this Institution.

J. Wilson Swan. G. D. Liveing. H. J. H. Fenton.
Chas. W. Low, M.B. John Percival. T. W. Easterfield.

Darling, Thos.,

1, Palace Street E., Berwick-on-Tweed.

Chemical Manufacturer. Studied Chemistry, and continue to do so. Apply the Science to my business.

W. Ivison Macadam. R. Greig Smith.
Stevenson Macadam. *Robert Irvine.*
Stevenson Macadam, jr.

Eastick, Charles E.,

Myrtle Bank, Leyton.

Chemist to Messrs. Martineau & Son's Sugar Refinery, Clyde Wharf, Victoria Docks, E. For two years Assistant Chemist at the

Chemical Works of the Gas Light & Coke Co., Beckton, E. For six years Chemist to Messrs. Abram Lyle & Sons, Sugar Refiners, London. Registered Teacher of the City and Guilds of London Institute on the subject of Sugar.

C. Haughton Gill.	B. E. R. Newlands.
Thos. D. Lichtenstein.	F. S. Adair Roberts.
John A. R. Newlands.	A. Boake.
Wm. Macnab.	*H. H. B. Shepherd.*

Elford, Percy,

Christ Church, Oxford.

Studying and Teaching Chemistry. Was elected to a Natural Science Scholarship at Christ Church in 1884. Became Demonstrator in the Christ Church Laboratory in 1887. Class I, School of Natural Science, 1882. Demonstrator in the Laboratory of Balliol College, 1890. Has lectured and taken private pupils; and has been working for two or three years on the Conditions of the Decomposition and Synthesis of Ammonia.

A. Vernon Harcourt.	John Conroy.	D. H. Nagel.
J. E. Marsh.	V. H. Veley.	Arthur Colefax.

Fulcher, Lionel William,

37, Melford Road, Lordship Lane, S.E.

Junior Assistant (Science Collections), South Kensington Museum. Bachelor of Science, University of London (Honours in Chemistry). Student of Chemistry (especially Physical and Inorganic).

T. E. Thorpe.	W. P. Wynne.	A. E. Tutton.
Chapman Jones.	William Tate.	J. Howard.
	Alfred C. Young.	

German, George, jun.,

Ashby de la Zouch.

Estate Agent. Member of the Royal Agricultural College (by examination) and Gold Medallist thereof; obtained Honours Certificates in Organic Chemistry and Agricultural Chemistry.

Edward Kinch.	James Muir.	T. A. Dickson.
J. Augustus Voelcker.	Arthur G. Bloxam.	*A. H. Church.*
R. Warington.	*J. H. Gilbert.*	*E. W. Voelcker.*

Hall, Alfred Daniel,

Martyr Road, Guildford.

Lecturer (Oxford Univ. Extension) for the Technical Ed. Committee of the County Council of Surrey. 1st Class Final Honour School (Chemistry) of Natural Science, Oxford, 1884. Science Master at Blairlodge School, N.B.; the Hulme Grammar School,

Manchester; and King Edward's High School, Birmingham. Author of *Exercises in Practical Chemistry:* Rivingtons, 1890.

William A. Tilden. Henry E. Armstrong.
G. Crewe Chambers Francis Jones.
R. L. Taylor. Percy Morton.

Heath, John William,

33, Upper Gloucester Place.

Chemical Assistant, Royal Institution. Has had great experience as an Assistant and has given valuable aid in all the original investigations conducted at the Royal Institution for the last ten years.

James Dewar. F. A. Abel. C. Meymott Tidy.
W. C. Roberts-Austen. G. D. Liveing. Ludwig Mond.

Hall, Archibald,

34, Bishopsgate Street.

Analytical Chemist. Late student Finsbury Technical College. Associate of Institute of Chemistry, 1890.

R. Meldola. A. Norman Tate. Edw. Rider Cook.
Henry J. Cook. F. G. Arsell.

Holliday, John,

7, Aglionby Street, Carlisle.

Chief Assistant for five years to Mr. J. Hepworth (Memb. Inst. Ch., President Incorporated Gas Institute, Engineer and Manager of the Carlisle Corporation Gas Dept.). Chemist (three years) Carlisle Corporation Gas Department (at Gas Works, Sulphate of Ammonia Works, and Sulphuric Acid Works). Teacher under Science and Art Dept. in Inorganic Chemistry.

Hugh Barclay. Wm. Foster. Chas. Armitage.
Stevenson Macadam. W. Ivison Macadam.

Leather, John Walter,

15, Bradgate Road, Catford, S.E.

Agricultural Chemist. Senior Assistant in Chem. Laby., Royal Agricultural Society. Doctor of Philosophy. Dissertation—"Die Pipitzahoïnsäure." Fellow of the Institute of Chemistry of Great Britain and Ireland. Five years Senior Assistant in Chem. Laby., Royal Agricultural Society.

J. Augustus Voelcker. J. H. Gilbert. Bernard Dyer.
E. W. Voelcker. Charles E. Cassal. Edward Kinch.

Ludlow, Lionel,

90, Walter Road, Swansea.

Analytical Chemist and Assayer. Served articles four years with Dr. Morgan, F.C.S., F.I.C., at the Technical Institute, Swansea.

Now Chemist to the Cape Copper Mining Co., at O'okiep, Port Nolloth, South Africa.

W. Morgan, Ph.D. John Ruffle. Rhys Charles.
Jas. S. Merry. *W. Terrill.*

Lennox, Robert,

3, Inverness Terrace, Putney.

Senior Chemical Assistant, Royal Institution. Experienced as an analyst. Conducted a large number of Gas Analyses for "Challenger" Reports. During the last ten years has given material assistance in the conduct of research at the Royal Institution.

James Dewar. F. A. Abel. C. Meymott Tidy.
W. C. Roberts-Austen. G. D. Liveing. Ludwig Mond.

Leffler, Rudolf Laurentz,

21, Havelock Street, Sheffield.

Analytical Chemist (Assistant), Messrs. Thos. Firth & Sons, Norfolk Works, Sheffield. Chemistry Student three years Firth College, Sheffield. Obtained "Honours Certificate" (Theo. and Prac. Chem. and Prac. Physics). Student two years Metallurgical Dept., Shef. Tech. School. "Honour Certificate" (Theo. and Prac. Metallurgy). City and Guilds Exams., "Honours" in "Iron and Steel" and "Fuel." Sci. and Art. Depart., "Honours" in Pract. Metallurgy. Two years and nine months Assistant, Messrs. Thos. Firth & Sons, Limited (Lab.).

W. Carleton Williams. L. T. O'Shea. James Taylor.
W. H. Greenwood. *Jno. E. Platts.*

Marshall, John Willis,

10, Palatine Square, Burnely.

Head Science Master of the Burnley Mechanics' Institution, and Lecturer in Chemistry (Theo. and Prac., Inorg. and Org.) and Physics. B.Sc. (Victoria) Ord. in Biology and Honours in Chemistry. Assoc. of Owens College. Member of the University of Marburg. Honours Cert. in Alkali Manufacture, City and Guilds of London Inst. Public Analyst.

C. Schorlemmer. Harold B. Dixon. Arthur Harden.
G. H. Bailey. G. J. Fowler.

McLaren, Daniel, B.Sc.,

30, Raleigh Street, Nottingham.

Science Master. (1.) Graduate in Science of St. Andrews University. Honours in Chemistry, Physics. (2.) "Forrester" Prizeman and first in 1st Class Honours in Chemistry Class at above University. (3.) "Neil Arnott" Prizeman, and first in 1st Class

Honours in Physics at above University. (4.) Demonstrator in Chemical Laboratory, St. Andrews University. (5.) Teacher of Mathematics amd Chemistry (Prac. and Theo.) in All Saints' Higher Grade School, Nottingham.

Thomas Purdie. William Marshall. Isaac Patchett.
Percy F. Frankland. *John G. Taylor.*

Morris, Joseph,

Stamford Street, Mossley, near Manchester.

Trained Certificated Schoolmaster and Science Teacher. Science Teacher, under Science and Art Department, in Chemistry, Animal Physiology, Hygiene, and Agriculture at Butterworth Newhey National Science and Art School, near Rochdale, Stalybridge Technical School, and Mossley Mechanics' Institute.

R. L. Taylor. John Howard. Robt. R. Rothwell.
Jno. Wiltshire. *C. H. Corbett.*

Naylor, William,

182, Newhampton Road, Wolverhampton.

Chemist at the Wolverhampton Corporation Sewage Works. Two years' experience as Chemist in the Laboratory of Wolverhampton Corporation.

E. W. T. Jones. Alfred Hill. E. Frankland.
A. Dupré. *John Angell.*

Newlands, William P. R.,

Rosa, North West Province. India.

Analytical Chemist. Was a student in the Chemical Laboratory of the Normal School of Science from February, 1882, to June, 1883, also attended the Lectures on Chemistry during the same period, and those on Physics from October, 1882, to January, 1883. Was Assistant Chemist to Messrs. James Gibbs & Co., Manure Manufacturers, in London, from September, 1883, to February, 1884, and from that time to May, 1887, sole Chemist to the Plymouth Works of the same firm. Was Principal Assistant in the Laboratory of Messrs. Newlands Bros. from June, 1887, to December, 1888. From that date and at present holds the appointment of Chief Chemist to the Sugar Refinery and Distillery at Rosa, North West Province, India.

E. Frankland. F. R. Japp. Percy F. Frankland.
C. R. Alder Wright. W. E. Halse. *W. T. Burgess.*
Arthur R. Ling. *Henry Bassett.* *Charles E. Groves.*

Neilson, Thomas,

26, Harrington Road, Workington, Cumberland.

Analytical Chemist to the Distington Hem. Iron Co., Limited,

near Whitehaven. Contributed an original paper to the *Chemical News*, 27th April, 1891, on the "Estimation of Sulphur in Coal," &c., together with a new process for the Estimation of Sulphur, and a comparison of various processes in Sulphur Estimation. Have been two years student with Dr. Clark, of Glasgow, and three years Chemist to the Distington Iron Co.

John Borland. John Clark. R. R. Tatlock.
Hugh Barclay. *W. MacKean.*

Priestley, Laurence,

Forest View, Noel Street, Nottingham.

Chemist's Assistant. One session at the University College, Nottingham, in the Government Service Classes; two sessions at the same College, studying for the Minor Exam. of the Pharmaceutical Society; one session at the Liverpool School of Chemistry; and one session at the South London School of Chemistry; passed the Major Exam. of the Pharmaceutical Society.

Frank Clowes.	J. Bernard Coleman.	R. Lloyd Whiteley.
John Muter.	W. Henry Dodd.	*Edgar B. Truman.*
Jno. R. Ashwell.	*John S. Ward.*	*H. Belcher Thornton.*

Sauyal, Abhayacharan, M.A.,

Benares, at present Allahabad (India).

Professor, Physical Science, Muir Central College, Allahabad (India). Obtained the degree of Master of Arts with Honours at the Calcutta University in Physical Science and Chemistry in February, 1879. Was appointed Assistant to the Professor of Physical Science, Muir Central College, Allahabad, in August, 1880, and worked for about five years under S. A. Hill, Esq., B.Sc.(Lond.), and Dr. Murray Thomson, M.D., where he acquired experience as an Analytical Chemist. In July, 1885, was appointed to take charge of the College Classes of the Queen's College, Benares. In 1889, officiated for some time as Professor of Physical Science, Muir Central College, Allahabad, and since September, 1890, has been filling the office of Professor of Physical Science, Muir Central College. (Both the Queen's and the Muir Colleges teach up to the M.A. standard.)

W. Venis.	Kanny Loll Dey.	Tarapusauna Roy.
Ramchandra Dutta.	*Preo Loll Dey.*	*John M. Thomson.*

Scott, Charles K.,

26, Pigott Street, Limehouse, London, E.

Chemist and Overseer, North Brazilian Sugar Factories Co., Brazil. Assistant Chemist, London Beet Sugar Assn., two years. Five years Chemist to Messrs. Fowler Bros. & Co., Sugar Refiners,

Orchard Place Refinery, Blackwall, E. Four years evening student of Chemistry, Finsbury Technical College.

John A. R. Newlands. B. E. R. Newlands.
Geo. Patterson. Arthur R. Ling.
R. Meldola.

Stephenson, Thomas,

Bellasis Road, Byculla, Bombay.

Pharmaceutical Chemist. Minor and Major Examinations, Pharmaceutical Society of Great Britain. Author of *Prescriber's Pharmacopœia* (Bombay), and of various papers on Pharmaceutical Chemistry published in the *Pharmaceutical Journal* (London), and in the *Indian Medical Record* (Calcutta).

D. B. Dott, F.R.S.E. Alex. Kinninmont. Thos. Maben.
Adam Gibson. Stevenson Macadam. D. S. Kemp.
Peter McEwan. *Alex. Crum Brown.* *M. Carteighe.*
John Attfield. *Thos. Tyrer.*

Thorp, Walter,

3, Melbourne Villas, Headingley, Leeds.

Bachelor of Science (London). Formerly Assistant to Prof. T. E. Thorpe, F.R.S., at the Yorkshire College, Leeds. Student in the laboratories of Prof. Smithells (Leeds) and Prof. Wm. Ramsay, F.R.S. (Univ. Coll., London). Medallist in Organic Chemistry, Univ. Coll., London, 1890.

T. E. Thorpe. William Ramsay. John Norman Collie.
R. T. Plimpton. Arthur Smithells.

Winterton, A. W.,

6, Lindum Terrace, Rotherham.

Metallurgical Analyst to the Parkgate Iron and Steel Co., Lim. Assistant Chemist and Steelmaker, Darlington Steel Co., 5 years. Manager of Testing Dept. (Physical and Chemical), Moor Steel Works, Stockton-on-Tees, 2 years. Chief Analyst, Parkgate Iron and Steel Co. (comprising mines, five blast furnaces, four Siemens' steel furnaces, refining, puddling, coke ovens, &c.), $1\frac{1}{2}$ years.

Bernard Dyer. John A. R. Newlands. W. E. Halse.
John Hughes. *Wm. Thos. Gent.* *Otto Hehner.*
Chas. Heisch. *Robert E. Moyle.* *Alfred H. Allen*

Wilson, John Henry,

29, Radford Street, Coventry.

Analytical Chemist. Associate of the Institute of Chemistry. "Tangye" Scholar in Chemistry, Mason Coll., 1890—91. Now en

gaged in Analytical and Research work under the direction of Prof. W. A. Tilden.

William A. Tilden.	W. W. J. Nicol.
T. Rhymer Marshall.	Thomas Turner.
J. J. Sudborough.	Chas. R. Beck.

Ward, Thomas Armistead,

Preston Road, Blackburn.

Manufacturing Chemist. Analyst to, and partner in, the firm of Clayton, Jowett, and Ward, Manufacturing Chemists, Liverpool and Blackburn. Associate of the Pharmaceutical Society (by exam.), having formerly studied Chemistry and Practical Chemistry under Professors Dunstan and Attfield.

Wyndham R. Dunstan.	John Attfield.
John W. Clayton.	W. Hall Jowett.
Robert G. Gow.	*Thos. Tyrer.*
John Hargreaves.	*Robert Yates.*

John Moss.

White, Henry,

8, Brown Street, Masboro', Rotherham.

Manufacturing Chemist. Seven years' experience in the manufacture of various commercial acids, cyanides, soaps, &c., &c. Science Certificates in Organic and Inorganic Chemistry.

J. O. Arnold.	C. Bradshaw.	Ed. Rawlins.
A. W. Duncan.	*B. W. Winder.*	*G. T. W. Newsholme.*

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Issued 1/12/1891.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 102. Session 1891–92.

November 19th, 1891. Sir Henry Roscoe, F.R.S., in the Chair.

Certificates were read for the first time in favour of Messrs. Hugh Brown Collins, West Balgray, Glasgow; Albert Henry Luckett, Brighton College, Brighton; James Hill Millar, 13, Waterloo Road, Wolverhampton; James Alexander Schofield, University of Sydney, New South Wales; Morris William Trewers, 2, Phillimore Gardens, Kensington, W.; Hugh Woods, 11, Archway Road, Highgate, N.

The following paper was read :—

67. "Iron carbonyl." By Ludwig Mond, F.R.S., and Dr. Langer.

The authors have isolated two compounds of iron with carbon monoxide, represented by the formulæ $Fe(CO)_5$ and $Fe_2(CO)_7$, for which they propose the names Ferropentacarbonyl and Diferroheptacarbonyl.

The ferropentacarbonyl is obtained by exposing finely-divided iron in an atmosphere of carbon monoxide at the ordinary temperature during about 24 hours, and then heating to about 120°. A small quantity (about 1 gram from 100 grams of iron) of an amber-coloured liquid is thus obtained, of the relative density 1·4666, which solidifies below −21°, forming acicular, yellowish crystals. The compound distils unchanged at 102·8°, the vapour having a density of 6·5, that corresponding to the formula $Fe(CO)_5$ being 6·7. It is not acted on by dilute acids; nitric acid, chlorine and bromine destroy it; alcoholic solutions of alkalis readily dissolve it, and form red-coloured solutions, which rapidly change in contact with air, but from which, as yet, no definite compounds have been obtained.

Diferroheptacarbonyl is obtained by exposing the liquid ferropenta-

carbonyl to light. It separates in gold-coloured crystals, carbon monoxide being liberated. The crystals are almost insoluble in all ordinary solvents; they are not volatile, but on heating to 80° they are decomposed into iron, ferropentacarbonyl and carbon monoxide. The crystals are not changed by dilute acids, but are readily acted on by nitric acid, bromine and chlorine. Alcoholic potash dissolves them, forming a red solution, very similar to the solution of the ferropentacarbonyl.

A lecture was then delivered on

"Colour-photometry." By Captain Abney, C.B., D.C.L., F.R.S.

Colour has been usually made the subject of reference to empiric and variable standards, a practice which affords results useless for future reference, and only suitable for present immediate wants. What is required is a reference to numbers which are on some standard scale that can easily be reproduced.

According to the lecturer, *the colour of a body, when viewed in a light of standard quality, is known when* (a) *its luminosity*, (b) *its hue and* (c) *its purity, or the extent to which it is freed from admixture with white light, are known and expressed by numbers.*

The luminosity of a colour can be given in absolute number by referring it to the standard of white. Thus, if white light fall on a coloured surface and on a surface of some standard white, the luminosity of the former may be expressed in terms of that of the light. It may appear difficult to compare the brightness of two such surfaces, but as a fact, the comparison is easily accomplished by causing the light falling on the white surface to be rapidly alternately made brighter and darker than that falling on the coloured surface. This can be done by interposing in the beam falling on the white surface rotating sectors with apertures which open and close *at will* during rotation. The point of equal luminosity can be found by this plan within 1 per cent. Experiments exemplifying the method were made, the brightness of an orange and of a blue pigment being compared with that of a zinc oxide surface which the author uses as standard white. It was also shown by sending the beams through a trough containing water in which mucin was suspended in minute particles, that the relation only held good for the particular light in which it was measured. Hence the necessity for using a standard light.

The luminosity of the light transmitted through coloured translucent bodies was also measured, and the same necessity shownfor the use of a standard light.

The standard light recommended was that from the crater of the positive pole of the electric light when high illumination was

required, or from a petroleum lamp when the illumination need not be so intense.

The method of measuring the luminosity of *light coming through translucent bodies* was also shown. A white oblong of paper was placed on a blackened card, a square which occupied half this oblong being pierced in the card, and thus half could be illuminated from the back of the card, and the other half by light from the front by placing a rod in the path of the beam to cast a shadow on the first half. The translucent substance was placed close behind the aperture in the card, and the light illuminating the paper, after passage through the translucent medium, was measured by altering the illumination of the other half lighted from the front.

The luminosity of the pure spectrum colours may be measured by what the author calls the colour patch apparatus, which is described in the *Phil. Trans.*, 1886, and in his work on "Colour Measurement and Mixture." It essentially consists of a collimator, two prisms, a lens, and a camera on the screen of which a spectrum is brought to a focus. This screen is removed for experiments, and a collecting lens used to recombine the spectrum, and to form an image of the last surface of the second prism on a screen some 4 feet off. A slide with a slit passed through the spectrum causes the white patch to become a colour patch of monochromatic light due to the particular ray traversing the spectrum slit. The white light with which the colour is compared is obtained from the light coming through the collimator and reflected from the first surface of the first prism; by means of a mirror and lens, it forms a patch equal in size to, and which can be caused to overlap, the coloured patch, or to lie alongside of it. In the first case, a rod placed in the path casts two shadows, one of which is illuminated by the colour and the other by the white light; rotating sectors in the path of the latter allow the luminosity to be compared. The light used is the electric light, an image of the crater of the positive pole being formed on the slit of the collimator.

The luminosity of a colour is not the same when viewed from all parts of the eye. The centre of the eye is that with which observations are usually made; hence the luminosity should be measured with that part of the retina, and it is advisable that no more than 6° of angular measure from the eye should be compared.

The audience were enabled to see the difference in luminosity of a colour which was of equal brightness to a certain white when viewed centrally, by shifting the axis of the eye so that the image was received on the retina some 10° away from the centre.

The action of the yellow spot was then alluded to.

The luminosity of any pigment on paper can be found by rotating it with two of the three colours: red, emerald-green and ultramarine.

These three make a grey which matches a grey formed of black and white. If the luminosity of the three have been accurately determined, by substituting the pigment whose luminosity is required for one of them, another grey can be formed to match a grey consisting of black and white. After measuring the angular aperture of the sectors, the luminosity is determined by calculation; the result is found to agree with the measurement made by the direct method. This is one of the many proofs that the measure of luminosity obtained in the manner described is correct, and not a mere accident.

The colour of a pigment can be referred to the spectrum colours by measuring the absorption. In the case of transparent bodies, this is best done by using a double-image prism at the end of the collimator so as to form two spectra on the camera screen. By adjustment, these may be caused to be so exactly one over the other, that the same colour will pass through a slit in them. After emergence from the slit, the rays from the top spectrum are diverted by a right-angle prism, and caught by another which sends them through a lens on to the screen, forming a patch. Another patch as usual is formed by the rays from the bottom spectrum. By placing the transparent body in the path of one of these rays, the absorption can be measured by equalising the brightness of the patches by the sectors and noting the apertures. The absorption of pigments can be measured in the same way by causing one patch to fall on the coloured surface and the other on the standard white.

To measure the absorption of pigments an easy plan is to rotate black and white sectors together with variations in the amount of white, and to cause the colour patch to fall partly on them and partly on the pigment. The colour is varied till it is seen that the grey disc and the pigment reflect the same amount of light.

By both these plans templates can be cut out, which, when rotated in the spectrum, give the exact colour of the pigment on the screen; hence this is a reduction of the true colour to absolute numbers, since the colour can be reproduced from a reference to a note book. It is to be remarked that the measures are unaffected by any defect in the eye of the observer or by the kind of light in which they were effected.

The mixture in varying proportions of red, green and violet of the spectrum makes white. This was shown by placing three slits in standard positions in the spectrum, and altering their apertures till a match was made with a patch of white light alongside.

Any other colour can be matched by the mixture of the same three colours, as was shown in matching green, blue, and brown papers.

Since three colours will make white, and the same three colours will make a match with an impure colour, every colour in nature can evi-

dently be matched by mixing not more than two of these colours with a certain proportion of white light; and if these colours be red and green, or green and violet, the colour can be matched by one spectrum colour and white light, since there is some intermediate colour which has the same hue as the mixture of these two colours. Hence any colour, except purple, can be referred to some spectrum colour, together with a certain proportion of white light. In the case of purple the colour may be expressed as white light, from which the complementary colour is eliminated. *Hence any colour whatever may be expressed in terms of white light and one spectrum colour, the latter in wave-lengths, and the former in percentage of luminosity.*

This was shown to be the case by interposing between the silvered mirror which reflected the light coming from the first prism, and which formed the white comparison patch, a plain glass mirror which reflected a small percentage of the light on to the colour patch, the amount of which could be regulated by sectors. Brown paper was placed in the white patch, and the spectrum colour was changed and mixed with the white light till the same colour was obtained. The scale of the instrument told the wave-length, and, by interposing a rod in the path of beams, the proportional luminosities of the spectrum colour and of the white light were determined. A similar match was made by light going through signal-green glass, and the complementary colour of the light passing through permanganate was determined.

Light coming through properly picked specimens of red, blue and green glass, and overlapping, may also be made to match a colour.

The three glasses covered a square lens, and formed an image on a screen of a circular patch of white light coming through ground glass on a screen. Colours were placed on a white beam alongside, and by altering the amount of the coloured glasses exposed, matches were made.

If the dominant wave-lengths of the colour of these three glasses be known, and also the amount of white light mixed with it, these measures can be noted in terms of these three glasses; and, further, it is possible, by mixing the light coming through the three glasses in various proportions, to obtain a spectrum colour mixed with white light for each such mixture. Hence this is a substitute for the spectrum itself. To show this, three similar glasses were placed over apertures suitably cut in a circular card; and, by causing these to rotate in front of an illuminated slit a sham spectrum was thrown on the screen in which every colour was present.

Any colour can be reproduced with three rotating sectors of red, green and blue when certain proportions of white or black, or both, are mixed with one or other. If the dominant wave-lengths and the proportion

of white light mixed are known of each such colour, the pigment whose colour is to be determined can be expressed in numbers as before, and in terms of spectrum colours if desired. This was shown by matching brown paper with red, blue and green, a little white and black being mixed with the brown.

The importance of using some uniform light was insisted upon throughout, slight deviations in the experiments demonstrating this.

In conclusion, Captain Abney claimed to have demonstrated that the reference of colour to numbers was not only possible but easy, and that, to chemists especially, the application was one of almost capital importance. Everyone could do it, and the lecturer had an instrument on the stocks which was not so cumbersome as that shown, but which would answer all purposes, he hoped, when complete.

RESEARCH FUND.

A meeting of the Research Fund Committee will be held in December. Fellows desiring grants are requested to forward their applications to the Secretaries before December 12th.

At the next meeting, on Thursday, December 3rd, there will be a ballot for the election of Fellows, the candidates being those whose certificates are published in No. 101 of these Proceedings, issued November 17, 1891.

The following papers will be read :—

1. "Phosphorous oxide. Part II." By Professor Thorpe and Mr. A. E. Tutton.
2. "Frangulin. Part II." By Professor Thorpe and Dr. A. K. Miller.
3. "The structure and chemistry of flames." By Prof. Smithells and Mr. H. Tingle.
4. "The composition of cooked vegetables." By Miss Williams.
5. "The occurrence of a mydatic alkaloid in lettuce." By T. S. Dymond.
6. "Some metallic hydrosulphides." By S. E. Linder and Harold Picton.
7. "The physical constitution of some solutions of insoluble sulphides." By Harold Picton.
8. "Solution and pseudo-solution." By Harold Picton and S. E. Linder.

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Issued 14/12/1891.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 103. Session 1891–92.

December 3rd, 1891. Professor A. Crum Brown, F.R.S., President, in the Chair.

Messrs. T. M. Wyatt and Peter MacEuan were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Frederick Edward Adams, Town Hall, Bolton; John Edward Whitley M. Fall, Bankfield Road, West Derby, Liverpool; John C. Hewlett, 40, Charlotte Street, E.C.; Robert Ludwig Mond, 20, Avenue Road, Regent's Park, N.W.; William Shields Myers, New York; George P. Daniell Smith, 26, Colebrooke Row, Islington, N.

The following were duly elected Fellows of the Society:—Harold Alger; George Alfred Ashcroft; George James Allen; Edward Charles Cyril Baly; Thomas William Berry; Samuel Francis Burford; John Bairstow; J. Treeby Barratt; John Redman Bovell; John C. Chorley; William A. S. Calder; George Edward Cory; Thomas Darling; Charles E. Eastwick; Percy Elford; Lionel William Fulcher; George German, Jun.; Alfred Daniel Hall; John William Heath; Archibald Hall; John Holliday; John Walter Leather; Lionel Ludlow; Robert Lennox; Rudolf Laurentz Leffler; John Willis Marshall; Daniel McLaren, B.Sc.; Joseph Morris; William Naylor; William P. R. Newlands; Thomas Neilson; Laurence Priestley; Abhayacharan Sauyal, M.A.; Charles K. Scott; Thomas Stephenson; Walter Thorp; A. W. Winterton; John Henry Wilson Thomas Armistead Ward; Henry White.

The following papers were read:—

68. "Phosphorous oxide. Part II." By T. E. Thorpe, F.R.S., and A. E. Tutton.

In this paper the authors continue their description of the properties of phosphorous oxide, P_4O_6. In their first communication (Trans., 1890, 553) it was stated that the oxide rapidly became red when exposed to light: they have since obtained phosphorous oxide in large, well-defined crystals, unaffected by light, by repeatedly exposing a quantity of the freshly distilled oxide to sunshine for several months at a time, and decanting the melted oxide from the red phosphorus produced. Large crystals of the oxide may also be obtained by spontaneous sublimation in a vacuum, which remain unaffected by light, so long as they retain their crystalline form; but if they are melted by the warmth of the hand, and then allowed to cool to the wax-like form, reddening occurs on exposure to light. Hence it appears not improbable that the permanency of the crystallised oxide is in some way connected with its crystalline character.

Bromine acts energetically on phosphorous oxide in a manner similar, in the end, to the action of chlorine. In a closed apparatus, however, an intermediate change occurs, crystals of phosphorus pentabromide subliming, and phosphoric anhydride being also formed, $5P_4O_6 + 20Br_2 = 8PBr_5 + 6P_2O_5$. The pentabromide is afterwards washed down by the excess of bromine, and acts on the phosphoric anhydride, the ultimate result being that products are obtained corresponding to the equation $P_4O_6 + 4Br_2 = 2POBr_3 + 2PO_2Br$.

Iodine acts more slowly than bromine, forming crystals of P_2I_4. The interaction is best carried out in carbon bisulphide solution in a sealed tube at a temperature of 150°: $5P_4O_6 + 8I_2 = 4P_2I_4 + 6P_2O_5$.

Hydrogen chloride gas acts on phosphorous oxide, forming phosphorus trichloride and phosphorous acid: $P_4O_6 + 6HCl = 2PCl_3 + 3H_3PO_3$. A subsidiary change also occurs between the two products of the reaction, with formation of more or less phosphorus, orthophosphoric acid and hydrogen chloride: $PCl_3 + 4H_3PO_3 = 3H_3PO_4 + P_2 + 3HCl$. On distillation a weight of phosphorus trichloride is obtained equal to that of the oxide employed.

When sulphur is heated with phosphorous oxide in a closed tube at about 160°, a most violent action takes place, the product of which is *phosphorus sulphoxide*, which is obtained in colourless, tetragonal crystals upon sublimation in a vacuum. The crystals melt at about 102°, and the liquid boils constantly at 295° (corr.). Vapour density determinations show that the molecular formula of the sulphoxide is $P_4O_6S_4$.

It is a highly deliquescent substance, which rapidly dissolves in water, forming at first meta-, and subsequently ortho-phosphoric acid

and hydrogen sulphide: $P_4O_6S_4 + 6H_2O = 4HPO_3 + 4H_2S$. It is also soluble in carbon bisulphide, from which it is again obtained upon evaporation in tetragonal prisms.

Sulphur trioxide is reduced by phosphorous oxide, the sole products being sulphur dioxide and phosphoric anhydride.

Sulphuric acid dropped upon phosphorous oxide occasions great rise of temperature; with quantities of a gram and upwards incandescence occurs. Sulphur dioxide is liberated, and phosphoric acid formed.

Sulphur chloride, S_2Cl_2, also acts with violence, forming phosphoryl and thiophosphoryl chlorides, sulphur and sulphur dioxide: $P_4O_6 + 6S_2Cl_2 = 2POCl_3 + 2PSCl_3 + 2SO_2 + 8S$.

Ammonia gas acts slowly in the cold, but with incandescence on warming to 30°. When ammonia is led over the oxide dissolved in ether, a white solid product is deposited, consisting of the diamide of phosphorous acid, $P(OH)(NH_2)_2$, and a small quantity of the corresponding ammonium salt: $P_4O_6 + 8NH_3 = 3P(OH)(NH_2)_2 + P(OH)_2(ONH_4)_2$. Phosphorous diamide is a white powder which is instantly dissolved by water with sufficient rise of temperature to induce incandescence. Treated with dilute hydrogen chloride solution, it evolves pure, non-spontaneously inflammable phosphoretted hydrogen, formed by the decomposition at the high temperature of the reaction of the phosphorous acid first formed: $P(OH)(NH_2)_2 + 2HCl + 2H_2O = 2NH_4Cl + P(OH)_3$.

Nitrogen peroxide vapour oxidises phosphorous oxide in the cold to phosphoric anhydride, being reduced to nitrogen tri- or di-oxide.

Phosphorus pentachloride acts with great energy on phosphorous oxide. The action may be controlled by cooling with ice. A liquid mixture of phosphorus and phosphoryl trichlorides is produced: $P_4O_6 + 6PCl_5 = 6POCl_3 + 4PCl_3$.

Phosphorus trichloride and phosphorous oxide only interact at a temperature near the boiling point (173°) of the latter, and in a closed vessel: under these circumstances, no phosphoryl trichloride is formed, but a solid mixture of pentachloride and pentoxide of phosphorus together with amorphous phosphorus.

Hydrogen, phosphoretted hydrogen, carbon monoxide, carbon dioxide, sulphur dioxide, nitrogen, nitric oxide, cyanogen and ethylene have apparently no action upon either cold or warm phosphorous oxide.

Discussion.

Professor Ramsay enquired on what grounds the authors came to the conclusion that the amide described was a phosphor*ous* and not a phosphoric compound, such as is represented by the formula $OPH(NH_2)_2$ corresponding to the formula $OPH(OH)_2$ for phosphorous

acid, which latter he thought was undoubtedly a phosphoric compound. The low boiling point and other properties of the sulphoxide described seemed to lend additional support to the view that phosphoric oxide was a compound of high molecular weight.

Dr. Armstrong remarked that the conventional view that the affinity of phosphorus for oxygen was very great was somewhat disturbed by the observations now described, showing that in many cases the phosphorus and oxygen in phosphorous oxide were readily separated; it would seem that the extreme stability of phosphoric oxide was probably conditioned by peculiarity of structure.

The authors, in their reply, said that they had no special experimental proof of the constitution of the diamide formed by the action of ammonia; Professor Thorpe, however, expressed the opinion that the balance of evidence was in favour of the view that phosphorous acid *is* $P(OH)_3$.

69. "Frangulin. Part II." By T. E. Thorpe, F.R.S., and A. K. Miller, Ph.D.

In the first communication to the Society by one of the authors, in conjunction with Mr. H. H. Robinson (Trans., 1890, 38), it was concluded that frangulin had the composition $C_{22}H_{22}O_9$. This conclusion was based on analytical results alone, and it was, in fact, pointed out that the percentage yield of emodin obtained on hydrolysing frangulin agreed better with Schwabe's formula $C_{21}H_{20}O_9$.

The authors have now prepared a larger quantity of frangulin, and have succeeded in obtaining it more nearly in a state of purity than was previously possible. They find, however, that crude frangulin contains a substance isomeric with emodin, which clings to it very persistently, and which it is very difficult to completely remove from the frangulin: they ascribe the conflicting statements of previous experimenters to the presence of this substance.

They have succeeded in proving the correctness of Schwabe's formula $C_{21}H_{20}O_9$. Their conclusions are based not only on their more recent analyses of frangulin, but also, and in fact mainly, on the esults obtained from the hydrolysis of frangulin. The two products of the hydrolysis are *emodin*, $C_{15}H_{10}O_5$, as shown in the first paper, and *rhamnose*, $C_6H_{12}O_5$. The latter substance was obtained in a crystalline form, and was identified by its chemical and physical properties and by the properties of its osazone. The percentage yield of emodin shows that one molecular proportion of frangulin yields one molecular proportion of emodin, and the difference represents one molecular proportion of rhamnose. It is thus possible to build up the formula of frangulin from its constituents, and since the result agrees

with the formula deduced from the analyses of the glucoside, the conclusion is justified that frangulin has the composition $C_{21}H_{20}O_9$, and that its hydrolysis takes place in accordance with the equation $C_{21}H_{20}O_9 + H_2O = C_{15}H_{10}O_5 + C_6H_{12}O_5$, which was given by Schwabe as highly probable.

The substance which has been mentioned as clinging so persistently to the frangulin has been isolated, and is found to have the same percentage composition as emodin. It melts at 202—203°, and is, without doubt, the same substance which Schwabe found and described as melting at 199°. It differs from emodin also in that it crystallises in golden-yellow needles, in the greater readiness with which it sublimes and in its reaction with alkalis. It is probably an isomeric trihydroxymethylanthraquinone.

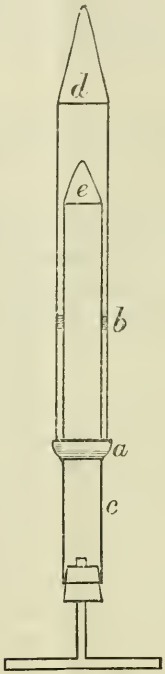
70. "The structure and chemistry of flames." By Arthur Smithells, B.Sc., and Harry Ingle, B.Sc., Yorkshire College, Leeds.

The authors have been engaged for twelve months in investigating the chemistry of flames produced by burning known hydrocarbons, and are still continuing their experiments. The publication of their results in the present form is consequent on the appearance of a paper by N. Teclu (*Journ. prakt. Chem.*, **44**, 246), who describes the phenomenon which served as a starting point in the authors' enquiry.

If a long glass tube be fitted by means of a cork over the metal tube of a Bunsen burner, so as to form a wider continuation of it, the flame can be caused to burn at the top of the glass tube. When the gas is turned slowly off, the flame becomes smaller, and develops a sharply defined inner cone of a greenish colour; this cone ultimately becomes almost a flat disc of flame and enters the glass tube. It will, as a rule, descend at a rapid rate for some distance, then begin to oscillate and finally either detonate and light the gas at the bottom of the metal tube, or else go out. If the gas supply be very carefully regulated, the flame may be got into such a state that it will descend the tube for a short distance and then re-ascend, and in this state it is very easy to see that whilst the lower cone is moving there remains at the top of the tube a steady cone of flame of a pale-lilac colour. By heating the glass tube at one point, so as to *increase* at that point the rate of inflammation, it is possible to fix the oscillating inner cone—that is, to prevent its *re-ascent*. It is also possible to effect this by narrowing the bore of the glass tube at one point, so as to *diminish* the rate of inflammation, *i.e.*, to prevent the *descent* of the inner cone past that point. In this way it is possible to separate the two hollow cones of combustion which constitute the Bunsen flame,

and to keep them any distance apart for any length of time. This permits of the aspiration of the gases from the space between the cones without any chance of admixture of outside air or of products of combustion from the upper cone.

The apparatus used by the authors in most of their experiments consisted of two glass tubes, one of which slides very easily within the other. The inner tube (*c*), which is the longer one, is united to the outer one by an india-rubber collar (*a*), through which it slides freely, and the two tubes are kept coaxial by a ring of asbestos packing (*b*). The projecting end of the inner tube may be fitted to a Bunsen



burner, but the authors have usually led separate supplies of gas and air into the apparatus by a T-tube, instead of using a Bunsen burner, in order to have a better control of the flame. With this apparatus a non-luminous flame is easily obtained, and the two cones can be separated in two ways. If the apparatus is arranged so that the flame is formed at the orifice of the wider tube (*d*) and the orifice of the narrower one (*e*) is 8 or 10 cm. below it, on increasing the air supply the inner cone of flame will ultimately descend and rest upon the orifice of the inner tube. If, on the other hand, the inner tube be

made to project beyond the outer one and the non-luminous flame be formed on it, then, if there be a sufficient air supply, on sliding up the outer tube it will as it passes the flame cleanly detach and carry up the outer cone, leaving the inner one still burning on the inner tube.

The authors have made similar experiments with flames of liquid hydrocarbons by charging air with the vapour of the liquid by passing it through a "saturator" such as is used for producing the ether-oxygen lime-light. The vapour-charged air is afterwards mixed with more air, and by suitably regulating the proportions a non-luminous flame is obtained and divided into two cones. In the case of liquid hydrocarbons, the lower cone of flame usually appears to be divided by dark spaces into several petal-like divisions which are in rapid rotation. In the case of benzene vapour the following sequence of appearances is presented: starting with the orifice of the inner tube, 8 or 10 cm. below that of the outer one, a luminous smoky flame is first obtained at the latter; as air is gradually added the flame becomes less and less luminous, and an inner cone begins to develop, but before this has become non-luminous it descends to the inner tube; more air makes both it and the upper cone non-luminous, and this state may be maintained. If now somewhat *less* air is supplied, a luminous streak appears at the tip of the inner cone, and passes right up and through the tip of the upper cone. If *more* air is supplied, the upper cone of flame begins to disappear, and only the upper part of it remains; this also gradually fades away, and then there is only the lower cone left. Still more air produces a visible effect on the inner cone, the colour changing and the combustion becoming less intense until the cone rises from its seat, passes upwards and disappears. There is thus a gradual transition from the richly luminous flame to one consisting of a simple pale-blue cone just on the point of extinction through excess of air.

The hydrocarbons examined by the authors were ethylene, methane, pentane, heptane and benzene. Coal-gas was also used. The gases from the regions between the two cones of flame were analysed in all these cases volumetrically or gravimetrically. The following are some of the results obtained:—

Substance.	C_2H_4.		CH_4.	C_5H_{12}.	C_7H_{16}.	C_6H_6.	Coal gas.		
	mm.	mm.	mm.				mm.	mm.	mm.
Diameter of outer tube	29	29	29	—	—	19	29	19·5	28
Diameter of inner tube	20	20	20	—	—	8	20	12	8
G (gravimetric) or V (volumetric).	G	V	V	V	V	V	G	V	V
CO_2	3·8	3·6	6·8	7·0	6·5	13·1	3·8	4·2	4·8
H_2O	9·5	9·5	17·6	13·1	12 3	7·7	14·9	16·0	15·9
CO	15·3	15·6	4·5	7·9	9·5	5·0	10·2	8·8	7·1
Hydrocarbons ...	0·8	1·3	—	—	—	0·6	—	—	—
H_2	9·5	9·4	3·9	5·4	5·8	0·64	10·9	9·3	7·7
N_2	61·1	60·6	67·2	66·2	65·6	73·1	60·3	62·0	64·4

These results, which are obtained in the preliminary survey, are not quite accurate owing to the impurity of the hydrocarbons and certain difficulties which are described in the paper. They show, however, that the products of combustion of the first cone are essentially CO_2, H_2O, CO and H_2, and that the second zone is due to the combustion of the CO and H_2 with the external air.

The results are in harmony with the conclusions of Blochmann, obtained indirectly, and with the not generally known work of Dalton on the explosion of methane and ethylene with oxygen in quantities insufficient for complete combustion, which was repeated in 1861 by Kersten.

The authors point out (i) that carbon, according to Baker's experiments, even in excess of oxygen, burns preferentially to CO, and not to CO_2; (ii) that the heat of combustion of gaseous carbon to CO is probably greater than that of hydrogen to H_2O; (iii) that, according to Dalton, CH_4 when burnt with its own volume of oxygen gives products represented in the equation $CH_4 + O_2 = CO + H_2O + H_2$; and they conclude that this equation represents the character of the change first taking place in the inner cone. But as the two substances CO and H_2O act upon one another ($CO + H_2O \rightleftarrows CO_2 + H_2$), the case is one of reversible change, and four products will result, viz., CO_2, H_2O, CO and H_2.

The conditions of equilibrium of this system, according to Dixon, are expressed by the coefficient $\frac{CO \times H_2O}{CO_2 \times H_2} = 4{\cdot}0$. This is subject to certain conditions of temperature and dilution. The authors in their most reliable experiments (viz., the gravimetric ones), with ethylene and coal gas, get numbers not greatly differing from 4; but they are still engaged in studying this question.

The authors have succeeded in dividing into two cones flames produced by admixture of air with cyanogen, sulphuretted hydrogen, carbon bisulphide and decomposed ammonia (*i.e.*, $N_2 + 3H_2$). The products of the inner cone in the case of cyanogen were found in one experiment to consist of CO and CO_2 in the proportion of 2 vols. of the former to 1 vol. of the latter.

Professor Smithells is continuing the experiments, with a view of elucidating the following points:—

(i.) The influence of differences of diameter of the tubes and rates of efflux on the fractional combustion.

(ii.) The exact composition of the interconal gases in the case of hydrocarbons, and also of mixtures of $CO + H_2$, so as to ascertain if, and in what way, the coefficient $\left(\frac{CO \times H_2O}{CO_2 \times H_2} = 4\right)$ varies with the composition of the gases and other conditions.

(iii.) The composition of the interconal gases from hydrocarbon flames whilst carbon is being liberated, so as to ascertain whether the luminosity of flames is due to simple decomposition of hydrocarbons by heat, to preferential combustion of hydrogen, to partial decomposition, or to other change.

(iv.) The exact nature of the flame of cyanogen, so as to ascertain what governs the proportions of CO and CO_2 formed in the inner cone.

(v.) The manner in which the partition of oxygen takes place in the inner cone between C and H, H and S, C and S, so as to obtain information as to the affinities of C, H and S for oxygen.

(vi.) The spectroscopic appearances of the flames.

Discussion.

Professor Thorpe, after expressing regret that time did not permit of the discussion of the numerous interesting questions which had been raised, referred to Professor Smithells' remark, that the books failed to notice the fact that carbonic oxide was produced on partial combustion of methane. He pointed out that Mr. Thomas, several years ago, made a special study of this question, having been led to do so by the observation that in cases of undoubted marsh gas explosions in coal mines the men killed often exhibited an appearance suggestive of carbonic-oxide poisoning. Mr. Thomas found that carbonic oxide and hydrogen were regular products of the incomplete combustion of marsh gas. (*Cf. Coal-mine Gases and Ventilation*, by J. W. Thomas. Longmans and Co., 1878. Also *Iron*, 1875).

71. "Note on the structure of luminous flames." By Arthur Smithells, B.Sc.

The author gives a brief summary of the various views that have been held on this subject. With one or two exceptions, there has been general agreement since the time of Berzelius that an ordinary candle flame, or the flame of coal gas escaping from a circular hole, is divisible into four chief regions: (i) the dark inner part; (ii) the luminous part; (iii) a small, bright-blue part at the base of the flame, thinning off rapidly as it extends upwards; (iv) a dim, scarcely visible, faintly luminous mantle surrounding the whole flame.

The explanation which the author would give of these regions is as follows:—The gas or vaporised wax, on issuing from the orifice or wick, becomes mixed with air and burns. Whether or not the flame is luminous depends on the rate at which the combustible is supplied. If slowly supplied, sufficient air is admixed with the gas for non-luminous combustion. Thus a very small gas flame is non-luminous, and so also the flame of a candle, with the wick cropped close to the wax. It is conventionally said that coal gas burns with a luminous flame; it is just as true to say that it burns with a non-luminous flame. The small, non-luminous flame of coal gas, or of a short wick candle, is seen to have the same structure as a Bunsen burner, viz., a bright-blue, inner cone, and a pale-lilac cone superposed upon it. The author supposes that we have here the same chemical changes occurring as are dealt with in the previous paper, viz., that the first combustion in the inner cone is mainly to CO_2, H_2O, CO and H_2, and the final one in the outer cone is mainly that of CO and H_2 to CO_2 and H_2O. This is made more probable by the fact that if the gas supply be increased, the luminous tip appears just at the point where it appears in the experiment with benzene, and that even after it is considerably developed the shape of the flame betrays the persistence of the inner cone. As the gas supply is further increased, the luminous area becomes increasingly great, the relics of the two original cones being very small.

The author's view is further enforced by the simple experiment of taking a flame about 5 cm. high from a Bunsen burner with the air holes stopped, noting the blue region at the base of the flame and the dim mantle outside it and then gradually turning on the air. The gradual transition shows unmistakably that the blue part and the mantle are the "rudiments" of the two cones of a Bunsen flame.

With regard to the luminous part, everything goes to show that it is mainly a region where hydrocarbons are decomposed by the heat of the outer parts of the flame. The precise nature of the change is being studied by the author.

The dark, inner zone contains mainly unburned gas, mixed with some products of combustion from surrounding regions.

A commonly held view that the mantle of a luminous flame is due to heated air and products of combustion is inconsistent with the above explanation, and also with the fact that in recent experiments it has been found impossible to render air luminous at the highest attainable temperatures.

The view that carbon is separated in a flame owing to the preferential combination of oxygen with hydrogen, is opposed, the author thinks, to all experimental evidence, which he is of opinion goes to show that if the oxygen supply be limited carbon will burn *before* hydrogen.

The author would describe a luminous flame as follows: —

(i.) An outer sheath or mantle, with (ii) an inner, bright-blue portion visible at the base of the flame. These two parts correspond respectively to the outer and inner flame cones of a Bunsen flame, and mark the region where the coal gas or candle gas is burning with a large quantity of air.

(iii.) The yellow, luminous part marking the region where the heat of the parts (i) and (ii) is decomposing hydrocarbons, setting free carbon, which rapidly glows and burns.

(iv.) The dark, inner region, consisting of unburned gas, mixed with products of combustion of surrounding parts.

Novelty is not claimed for this description, but the author considers that the experiments described in the preceding paper put the matter in a somewhat new light.

72. "The existence of hyoscyamine in lettuce." By T. S. Dymond.

Lettuce has been used in medicine from early times as a sedative, but the active constituent has never been with certainty determined. The author's attention was drawn a few months ago to the mydriatic action of an extract of lettuce used in medicine. It had been prepared from the flowering plant of common lettuce according to the directions of the *British Pharmacopœia*. An examination showed that the mydriatic action was due to an alkaloid. Commercial specimens of the extract of wild lettuce and of the variety of the edible plant known as cos lettuce, obtained from three different sources, together with a specimen of the dried flowering plant of wild lettuce, were all found to contain this alkaloid.

The alkaloid was most easily isolated by mixing the commercial extract with water acidified with acetic acid, adding alcohol till precipitation of nearly all the constituents of the extract occurred, filter-

ing, evaporating the filtrate to a low bulk, filtering again, washing the filtrate with ether till free from fat, then rendering it alkaline and extracting the alkaloid with ether. The impure alkaloid thus obtained was purified by conversion into the oxalate, and the precipitation of this salt by ether from its alcoholic solution. On recovering the alkaloid and crystallising it from chloroform, it was obtained in silky needles having approximately the same melting point and other properties as hyoscyamine, the poisonous mydriatic alkaloid existing in belladonna, henbane and other plants belonging to the natural order *Solanaceæ*.

The identity of the alkaloid with hyoscyamine was confirmed by conversion into the aurichloride which melted at 159·75°, the melting point given by Ladenburg for hyoscyamine aurichloride being 159°. The determination of the gold and the alkaloid in the compound afforded results corresponding with the formula of hyoscyamine aurichloride, $C_{17}H_{23}NO_3 \cdot HAuCl_4$.

The amount of hyoscyamine in the extract of common lettuce does not exceed 0·02 per cent., while in the flowering plant itself, it cannot be more than 0·001 per cent. It appears that this is the first occasion on which hyoscyamine or any other alkaloid belonging to that mydriatic group has been found in a plant not a member of the natural order *Solanaceæ*, lettuce belonging to the natural order *Compositæ*.

Discussion.

Professor Dunstan pointed out that it had been known from the time of the Greeks that lettuce had a soporific action, and as Ladenburg and others had shown hyoscyamine to be a soporific, it was now possible for the first time to explain an ancient Grecian practice.

73. "Cryptopine." By D. Rainy Brown and W. H. Perkin, Junr., Ph.D., F.R.S.

The authors have commenced an investigation on the rare alkaloid cryptopine, which occurs in small quantity in opium, and which was first isolated by J. and H. Smith (*Jahresbericht*, 1867, 523), and subsequently analysed by Hesse (*Annalen*, Suppl. **8**, 209).

Analyses of the base and of several of its salts led Hesse to assign to cryptopine the formula $C_{21}H_{23}NO_5$. The authors have prepared and analysed several samples which had been purified by conversion into the oxalate and subsequent recrystallisation from isobutyl alcohol. The mean result of five analyses was—

		Theory for $C_{21}H_{23}NO_5$.
C	68·23 per cent.	68·29 per cent.
H	6·34 ,,	6·23 ,,
N	4·15 ,,	3·79 ,,

The oxalate, after repeated recrystallisation from water, was obtained in the form of beautiful glistening prisms, which, on analysis, gave the following numbers as the mean of four experiments:—

		Theory for $C_{21}H_{23}NO,C_2H_2O_4$.
C.....	59·82 per cent.	60·13 per cent.
H.....	5·55 „	5·44 „
N.....	3·31 „	3·05 „

These analyses confirm Hesse's results, and show that cryptopine has the formula $C_{21}H_{23}NO_5$.

On oxidation with potassium permanganate, cryptopine yields among other products a crystalline acid, $C_{10}H_{10}O_6$, m. p. 179—180°, which proves to be metahemipinic acid, $C_6H_2(CH_3O)_2(COOH)_2$ [1 : 2 : 4 : 5], the acid which Goldschmidt obtained from papaverine; this result is interesting in view of the fact that metahemipinic acid, up to the present time, has only been obtained from papaverine.

The identity of the acid obtained from cryptopine with that from papaverine was proved by the fact that both yield an anhydride, $C_{10}H_8O_5$, m. p. 175°, and an ethylimide, $C_{12}H_{13}NO_4$, melting at 226°.

Cryptopine contains only two methoxy-groups, as shown by its behaviour when treated with hydrogen iodide, these two groups being situated in that part of the molecule which is converted into metahemipinic acid on oxidation.

74. "The action of sodium on ethereal salts. Part III. Benzylic orthotoluate." By W. R. Hodgkinson.

The behaviour of the different ethylic toluylates towards sodium was briefly referred to in these Proceedings in 1886 (p. 188).

In all cases their behaviour is different to that of the ethylic salts of phenylacetic acid. No trace of any substituted acetic or benzenoid fatty acid could be found, and the action differs moreover in that no ring condensation appears to take place as is the case with ethylic phenylacetate, which affords "triphenylphloroglucol".

In the case of the benzylic salt of orthotoluic acid, it was thought that either the CH_2 might act in a similar manner to the CH_2 in phenylacetic acid, or that two molecules would condense, forming dimethylanthraquinone and benzylic alcohol.

Benzylic orthotoluate, $C_6H_4Me{\cdot}CO_2{\cdot}CH_2Ph$, which does not appear to have been previously formed, is a liquid of very pale-yellow colour which boils without the least decomposition at 315° (thermometer in vapour). Rel. den. at 17° 1·12.

As mentioned in connection with triphenylphloroglucol, the pro-

ducts of the action of sodium on these ethereal salts differ considerably according to the conditions of the experiment. On adding the sodium to the oil previously heated to 200° it dissolved, and the temperature rose to 250°, when an oil distilled over. This, on fractional distillation, separated into toluene and benzyl alcohol for the most part, with a smaller quantum of the original ethereal salt. The sodium salt in the retort dissolved in water, and gave on treatment in the usual manner an oil and an acid. This acid is *pure* o-toluic acid. The oil was found to consist of unchanged benzylic orthotoluate and a substance boiling at 350° (nitrogen thermometer in vapour) 360°.

This substance remained liquid at −10° and could scarcely be a derivative of anthraquinone. Analysis shows it to have the composition $C_{22}H_{20}O_2$, which is that of a substance of the formula $C_6H_4Me{\cdot}CO_2{\cdot}CHPh(CH_2Ph)$.

The quantity at present disposal has allowed only of hydrolysis with potassium hydroxide, from which it appears that *only* o-toluic acid is formed, and an oil which boils at about 250—280°. The matter is still under investigation.

75. "The gas-volumeter and gravivolumeter. By G. Lunge.

In this note the author comments on Professor Japp's reply to his criticisms (*Ber.*, **24**, 1656).

76. "The action of sulphuric acid on the bromides of hydrogen, potassium and sodium." By F. T. Addyman, B.Sc.

The author has sought to determine the extent to which hydrogen bromide is oxidised by sulphuric acid under varying conditions of mass and dilution.

He first describes experiments in which sulphuric acid ($d = 1{\cdot}84$) was allowed to act on potassium bromide, from which he infers that the amount of decomposition which the hydrogen bromide undergoes is very nearly proportional to the amount of sulphuric acid used; but it is subsequently admitted that the extent to which the hydrogen bromide and acid come into contact greatly affects the result, so that a higher percentage would be decomposed in a deep than in a shallow vessel.

In the second section of the paper, a method of preparing a solution of hydrogen bromide is described, very similar to that of Feit and Kubierschky (*C.S. Abstracts*, 1891. 1320). An account is then given of observations on the amount of change produced by sulphuric acid in solutions of hydrogen, potassium and sodium bromides. But mere traces of bromine are liberated in solutions containing not more

than about 30 per cent. of sulphuric acid; and the percentage of hydrogen bromide decomposed is but small, even when as much as about 70 per cent. of sulphuric acid is present.

77. "The iodometric estimation of chlorates." By G. McGowan Ph.D.

Attention is called to Finkener's statement, that when Bunsen's method is applied to chlorates, less than the theoretical amount of chlorine is evolved. Experiments are then described, made in accordance with the method, and with the apparatus of which an account is given at pp. 530—536 of this year's volume of the Society's Transactions, which corroborate the results of de Koninck and Nihoul, and prove the accuracy of the Bunsen method; Finkener's error doubtless arose from a slight loss of chlorine. The author emphasises the importance of carrying out all such determinations in an apparatus in which the chlorine does not come into contact with india-rubber.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Laboratory Practice: A Series of Experiments on the Fundamental Principles of Chemistry, by J. P. Cooke. New York 1891.
From the Author.

Reprints of Three Editorials regarding the Priority in Demonstrating the Toxic Effect of Matter accompanying the Tubercle Bacillus and its Nidus. Philadelphia 1891.
From the Bacteriological Laboratory, Acad. Nat. Sci. Philadelphia.

The Organic Analysis of Potable Waters, by J. Blair. 2nd Edition 1891. From the Publishers.

The Chemistry of Illuminating Gas, by N. H. Humphreys. London 1891. From the Author.

Quantitative Chemical Analysis, by F. Clowes and J. B. Coleman. London 1891. From Professor Clowes.

Engineering. Vols. III to XLIV. London 1867—1887.
From Dr. W. S. Squire.

The Principles of Chemistry, by D. Mendeléeff. Translated from the Russian (3rd Edition) by G. Kamensky and edited by A. J. Greenaway. 2 vols. London 1891. From the Publishers.

The Alkali-Maker's Handbook, by G. Lunge and F. Hurter. 2nd Edition. London 1891. From the Publishers.

Examinations by the State Board of Health of the Water Supplies and Inland Waters of Massachusetts 1887—1890. Parts I and II. Report on Water Supply and Sewerage. Boston 1890.

From R. Warington, Esq.

At the next meeting, on December 17th, the following papers will be read:—

1. "The composition of cooked vegetables." By Miss Williams.
2. "Some metallic hydrosulphides." By S. E. Linder and Harold Picton.
3. "The physical constitution of some solutions of insoluble sulphides." By Harold Picton.
4. "Solution and pseudo-solution." By Harold Picton and S. E. Linder.
5. "The change proceeding in acidified solution of sodium thiosulphate when the products are retained within the system." By Dr. A. Colefax.
6. "The action of sulphurous acid on flowers of sulphur." By Dr. A. Colefax.
7. "The α- and β-modifications of chlorobenzene hexachloride." By Dr. Matthews.
8. "Camphrone, a product of the action of dehydrating agents on camphor." By Drs. Armstrong and Kipping.
9. "Studies of the dibromonaphthalenes." By Dr. Armstrong and Mr. Rossiter.

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Issued 31/12/1891.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

No. 104. Session 1891–92.

December 17th, 1891. Dr. W. H. Perkin, F.R.S., in the Chair.

Messrs. William A. S. Calder, Arthur Colefax, Charles E. Eastick, Henry C. Jenkins and Thomas Neilson were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Arthur Adams, Broomfield Place, Smethwick; Francis V. Darbishire, 59, Elienstrasse, Dresden; James Hendrick, Laurel Cottage, Watermoor, Cirencester; Henry Hollingshurst, 2, Jentha Road, East Hill, Wandsworth; Frank William Lucas, M.A., 183, Belle Vue Road, Leeds; Ernest John Parry, B.Sc., Brooklands, Bensham Manor Road, Thornton Heath; William Pullinger, 27, Queen's Road, Oldham; Charles F. Seymour Rothwell, 82, Manson Street, Manchester; Thomas John Buckler Sandercock, Sidcup College, Sidcup, Kent; Henry John Spray, 15, Bucharest Road, Wandsworth; Alfred James Squires, 16, Lower Road, Newark, Notts.

Of the following papers those marked * were read :—

75. "The 'gas-volumeter' and 'gravivolumeter.'" By G. Lunge (*cf.* these Proceedings, *ante*, p. 168).

In the Proceedings of this Society (No. 96, April 4, 1891), Professor Japp describes an instrument by means of which the observed volume of a single gas gives directly the weight of the gas. This instrument is based on the principle of reducing gases to a standard volume by means which are the same as those I first introduced in the "gas volumeter," but Professor Japp prefers to call it by another name "gravivolumeter." To this I objected in a brief note in the *Berichte* (**24**, 1656), and Professor Japp has since replied in the last part of

his full paper published in the Transactions of the Society (1891, **59**, 894).

If it were merely a question of the name of an apparatus, I should not trouble the Society, as I have nothing to add to what I then said in the *Berichte*, leaving it to others to choose between the names in question. But in his answer to my objections Professor Japp has charged me with making contradictory statements and ignoring "a commonplace of physical measurement;" this compels me to ask the Society to publish my refutation of these charges.

In the *Berichte* (*loc. cit.*), I stated that the "gravivolumeter" is in point of fact absolutely identical with the "gas volumeter," but that by modifying the form of the regulator ("Reductionsrohr") which I prefer, Professor Japp has diminished the accuracy of the instrument. He remarks: "I fear I must leave Professor Lunge to reconcile these two statements." If he had referred to my original descriptions in the *Berichte* (dated February 14th, 1890) and the *Zeitschrift für angewandte Chemie*, (March 1st, 1890), he would have had no difficulty in doing so.

My regulator contains a certain volume of air, which under "standard" conditions causes the mercury to rise to a fixed point, and by producing this condition simultaneously in the regulator and the gas-burette, I reduce the gas contained in the latter to standard conditions also, thus avoiding in the measurement of the gas the necessity for observations of temperature and barometric pressure and all calculations connected therewith. My apparatus has completely realised this object, and Professor Japp has adopted the self-same principle and availed himself of the same means for effecting the reduction. It is manifestly indifferent, as far as the principle is concerned, whether the standard volume of air in the regulator is 25 c.c., or 50, or 100, as I have distinctly stated in a passage possibly overlooked by Professor Japp (*Ber.*, **23**, 444, line 30). For the sake of obtaining more accurate results, I preferred in practice to take 100 c.c., and to contract the tube below this point, in order to get larger divisions, but I did not confine my apparatus to any such special form. On the contrary, I showed, even in my first communication, several modifications of the regulator (with cylindrical top, with bulb top, with tap, and with a capillary); I also said (*loc. cit.*, p. 444, line 24): "I quote, of course, these combinations, to be varied at will, merely as *examples* how the apparatus may be arranged," and in the *Zeitschrift für angewandte Chemie*, 1890, pages 140 and 144, I remark that any "nitrometer" (*a fortiori* any "gas-burette") "may serve the purpose of a regulator." Consequently, when he adopted for this purpose an ordinary 50 c.c. gas-burette, Professor Japp did not introduce *any modification* in the principle of my "gas volumeter," but merely selected one out

of the various forms which would at once occur to any chemist on reading my description, although certainly not that which admits, in my opinion, of the greatest accuracy in working. I think this explanation will suffice for the reconciliation of my two statements.

As already stated, I have objected to a new name being given to an instrument identical with the one invented and named by myself, except that the readings are taken in a new way; but since then I have met with another reason why the name "gravivolumeter" should not be applied to the instrument. That name was bestowed years ago by Houzeau on another instrument of totally different principles and use (*Compt. rend.*, **88**, 747, and **90**, 870), and it would be likely to cause great confusion if designations previously proposed for totally different instruments were applied to new ones.

Professor Japp further says: "The acknowledgments of obligation throughout my entire note could hardly have been more profuse." But he seems to have overlooked the following passage at the end of my first paper in the *Berichte* in which: "*I reserve to myself the further extension of the principle embodied by my gas volumeter*, in this and in other directions, as well as the improvement in detail of the instruments shown here only in outline; but *I shall be grateful for any suggestions on the part of other scientists.*" In the *Zeitschrift für angewandte Chemie*, 1890, 142, more than a year before Professor Japp's first note, I repeated the above, adding that I intended to employ the name "gas volumeter."

Professor Japp admits that I have priority in the principle of reading off volumes of gases directly as weights, as when employing the gas volumeter for the estimation of nitrogen in organic combustions and for vapour densities. I had further claimed that I had attained the end of reading off volumes of gas directly as weights, by employing a certain weight of the substance to be analysed. To this Professor Japp objects that I do not find absolute weights, but merely percentage weights. Literally this is correct; but, as in almost all cases it is not the absolute but the percentage weights which are required, I fail to see the force of Professor Japp's objection.

I fully acknowledged the "sinnreiche Idee" of Professor Japp. which realises one of the "further extensions" of my principle foreshadowed in the above-mentioned passage of my first paper; but I ventured to submit, firstly, that it was not called for except in a limited number of cases, secondly, that it involved a loss of accuracy in the reducing operation. Both of these assertions I must maintain.

As for the first, I had already provided for all ordinary cases. In gas analysis proper, the reduction of volumes to weights is only quite exceptionally called for; in the gas-volumetric analysis of solid or

liquid substances, the direct estimation of the percentage weight by my method is a distinct advantage over that of the absolute weights as shown above; and for the estimation of nitrogen and vapour densities it is necessary to employ, in lieu of gas-burettes, specially constructed instruments, as described in my former papers.

According to my second criticism, Professor Japp's special form of regulator admits of only $\frac{1}{4}$th (perhaps even $\frac{1}{8}$th) of the accuracy yielded by the form which I prefer. This he tries to refute by taxing me with ignorance of "a commonplace of physical measurement," namely, that there is no advantage in making one of the interdependent parts of a determination much more accurate than another; but he is in error, for he assumes that I generally work with a 50 c.c. gas burette, whilst, as a matter of fact, I prefer, wherever possible, to work with far greater volumes, for which purpose the gas-burettes, as shown in my various papers, are constructed to hold up to 150 c.c. An uncertainty of 1/20th in 100 with the large gas-burette is exactly the same as in my regulator, namely, 1/2000th, as against 1/500th, the probable error with Professor Japp's regulator, "calculated on the basis of 25 c.c. as the average amount of gas measured." By means of a small movable straight edge, combined with a spirit level (the description of which I shall shortly publish), I can attain such accuracy in levelling the mercury in both tubes that the above minimum of error is actually realised. Even with 50 c.c. of gas in the burette, the accuracy is $\frac{1}{50 \times 20} = \frac{1}{1000}$th. This is, I think, sufficient refutation of Professor Japp's charge of ignoring "a commonplace of physical measurement."

I will lastly explain a passage in my note in the *Berichte* which Professor Japp seems to have misunderstood, the fault being doubtless attributable to the extreme conciseness of that note. I there said that by employing a volume of 25 c.c. only, in the regulator, the accuracy of reading is *a priori* reduced to $\frac{1}{4}$th, and, on account of the inconvenient form of the tube, probably even to $\frac{1}{8}$th. The "inconvenient form" is that of a cylinder of equal width throughout as compared with that of an instrument bulged out at the top, in which only the bottom part is cylindrical and graduated, and the divisions may therefore be much larger than in the former case. In England, the bottom part need only hold 10 or 15 c.c.; at Zurich or Munich, 20 c.c. A 50 c.c. burette would have to be made very inconveniently long, if equally large divisions (easily readable to 1/40th) had to be provided.

*78. "The composition of cooked vegetables." By Miss K. J. Williams.

The vegetables examined after cooking were :—Artichoke (Jerusa-

lem), broad bean, haricot bean, beetroot, cabbage, carrot, cauliflower, celery, cucumber, lettuce, mushroom, onion (Spanish), parsnip, pea (green), potato, radish, salsify, scarlet runner, sea-kale, spinach, tomato, turnip and vegetable marrow.

Determinations were made in these of the following :—

Water.
Carbon and hydrogen.
Nitrogen (total) by Dumas method.
Nitrogen by soda-lime combustion.
Nitrate extracted by dilute alcohol.
Ashes.
Sulphur.
Woody fibre by digestion with dilute sulphuric acid, &c.
Cellulose by Schulze's potassium chlorate method.
Carbohydrate convertible into glucose.
Fat.
Heat of combustion.

The results are given in a series of tables.

Discussion.

Mr. Warington remarked that the determinations of the heat of combustion were of considerable value, as these were the only data on which, at present, a comparison of the relative values of the different foods could be based ; to which Dr. Armstrong objected that the value of a vegetable food must depend both on the amounts of carbohydrates and albuminoids present and on their character, and therefore it did not seem probable that the determination of the heat of combustion would be of such special value. Mr. Warington then pointed out that the quantity of albuminoids required for the renovation of tissue in the human body was so small (at most 40 grams per day) that it could hardly fail to be present in an ordinary mixed diet ; unless, therefore, an increase were being made to the nitrogenous tissues, the value of a food practically depended upon the amount of heat which it could generate in the body, a remark which the Chairman subsequently said his experience of vegetarian diet enabled him to corroborate.

Dr. Kipping asked whether any attempt had been made to determine the effect on their composition of alterations in the mode of cooking vegetable foods.

Professor Ramsay, who had given an account of the paper, said in reply that in his opinion more value would attach to the determinations of heats of combustion if the digestibility of the foods had also been ascertained. As to the influence of modes of cooking, considerable

differences had been noticed by Miss Williams between potato boiled in the skin and without skin, but this was the only case hitherto studied.

*79. "Metallic hydrosulphides." By S. E. Linder and Harold Picton.

The authors have investigated the sulphides of copper, mercury, arsenic, antimony, cadmium, zinc, bismuth, silver, indium and gold (*cf.* these Proceedings, 1890). With the single exception of bismuth, all these metals form hydrosulphides of a more or less complicated character, which, in most cases, undergo molecular condensation with elimination of sulphuretted hydrogen when submitted to the action of acids. Taking copper as a type, on treatment with sulphuretted hydrogen, copper hydrate forms a *solution* of the hydrosulphide $7CuS,H_2S$. Acetic acid, in presence of excess of sulphuretted hydrogen, promotes molecular condensation, a product being formed which has approximately the composition $9CuS,H_2S$; while acetic acid, in absence of sulphuretted hydrogen, promotes the formation of a product approximately represented by the formula $22CuS,H_2S$. Chlorhydric acid produces still further condensation. Mercuric sulphide forms products approximately represented by the formulæ $31HgS,H_2S$; $62HgS,H_2S$. The latter formula represents the precipitate formed in presence of acid, and is a remarkably stable substance. Zinc sulphide solution obtained from the hydrate contains about 14 per cent. excess of sulphur as sulphuretted hydrogen; in presence of acetic acid, a product represented approximately by the formula $12ZnS,H_2S$ is formed.

The authors regard their results as evidence tending to support the conclusions that the metallic sulphides are in most cases polymerides of very high molecular weight.

*80. "The physical constitution of some sulphide solutions." By Harold Picton.

The author has specially examined the solutions of mercuric, antimonious and arsenious sulphides. In each case the whole of the dissolved sulphide is found to be present in the form of very finely divided particles. Arsenious sulphide is found capable of existing in "solution" in three distinct types of sub-division. The following examples illustrate the main characteristics of sulphide "solutions":—

Mercuric sulphide.—Particles are visible under the microscope (1000 diameters); is not diffusible even in absence of a membrane.

Arsenious sulphide (α).—Particles are just visible.

Antimonious sulphide.—Particles are not visible and it is not diffusible, but particles are detected by their power of scattering light, the scattered light being polarised.

Arsenious sulphide (β).—Not diffusible; the particles scatter and polarise light.

Arsenious sulphide (γ).—Diffusible in the absence of a membrane; particles are shown to exist by optical behaviour.

The solutions examined exhibit a series passing from those in which the particles of the solid are visible to those in which the particles simulate the phenomena of liquid diffusion, and, although not visible to the eye, are detected by their power of scattering light.

*81. "Solution and pseudo-solution. Part I." By Harold Picton and S. E. Linder.

The authors advance what they regard as a good *primâ facie* case for the belief that there is a continuous series of grades of solution passing without break from suspension to crystallisable solution. They hold that in the lowest grades of solution a certain loose attraction exists between the particles and the molecules of the solvent. This conclusion they support with experimental evidence gathered from their own work and from other sources. They regard the very finely divided particles in the lower grades of solution (colloid solution) as large molecular aggregates retaining many of their molecular properties. They consider that in passing up through the different grades of solution, these aggregates on the whole become smaller and the forces by which they are held in solution become more definitely those of chemical attraction. They describe a new property, which seems to hold for a large range of solutions, extending from suspension to crystallisable solution. This property consists in the repulsion of the dissolved substance, *as a whole*, from one of the electrodes of a battery immersed in the solution. Thus, in the case of colloidal arsenic sulphide, the sulphide aggregates are repelled from the negative electrode. They are also repelled, but much less strongly, from the positive electrode. In the case of the crystallisable colouring matter Magdala red in absolute alcohol, an exactly similar phenomenon is observed, but the repulsion is this time from the positive electrode, and there is no perceptible repulsion from the negative electrode at all. The property is of much interest in itself, but also as exhibiting similarities between the different grades of solution.

Discussion.

Mr. Page suggested that observations on the nature of solutions, such as those described by the authors, might with great facility be carried out in capillary tubes under the microscope.

Mr. Walenn said that in working with electro-coppering solutions containing resin in suspension he had had occasion to notice a clearing of the liquid at the anode, such as had been referred to.

Professor Ramsay said that the problem of Brownian motion, or pedesis, had engaged his attention since 1878, when he published a paper in the *Proceedings of the Geological Society* bearing on the settling of mud in salt water. The problem attacked by Messrs. Linder and Picton was one in which he thought pedesis played an all-important part, as the small particles, the existence of which had been proved by their power of polarising light, were in exceedingly rapid motion. Messrs. Linder and Picton had shown that there is a regular transition from visible particles to particles or molecules such as those of oxyhæmoglobin. It must, therefore, be concluded that such exceedingly small particles are also in rapid motion; and the smaller the particle, the more rapid the motion. Pedesis had not received, as yet, any satisfactory explanation; the only fact which appeared to throw any light on its nature was that the addition of a salt to the solvent, rendering it an electrolyte, hindered pedesis, and finally caused coagulation and settling. The discovery of the true nature of pedesis would in all probability be the key to the problem of the nature of solution.

Mr. Warington pointed out that the coagulation of clay by salts had been studied by Schloesing (*Chimie Agricole*, p. 62; Fremy's *Encyclopédie*, tome x) and W. Skey (*Chem. News*).

Mr. Herbert Jackson said that the phenomena discovered by the authors were similar to those observed in the case of the liquids produced during the washing of many precipitates, such, for instance, as lead hydrate or silver nitroprusside, which refuse to settle completely as soon as the liquid in which they are diffused becomes approximately pure water, or which show a tendency to come through the paper when washed on a filter. Such precipitates can be made to furnish turbid liquids in which the particles are so fine that they will not settle for many months, although, as is well known, the addition of a drop or two of a saline solution, *e.g.*, sodium acetate or potassium nitrate, will cause rapid deposition of the solid.

These opalescent liquids give the results described and shown by the authors when examined at right angles to a narrow beam of strong light.

He had found in the case of lead hydrate that the microscope revealed moving particles with an average diameter of 1/35,000 of an inch. Some, in the case of silver nitroprusside, were less than the 1/100,000 of an inch. The limit of separation with lenses and
nators giving the greatest possible angle for water immersion (viz., 1·33 numerical aperture is:—

For λ 5269	128,225	lines to the inch.
,, λ 4861	138,989	,, ,,
,, λ 4000	168,907	,, ,,

In the case of particles separated from one another by considerable intervals, these limits will be exceeded, as the dark diffraction outlines will give an apparent measurement of the particles distinctly greater than they really are; but it is quite clear that it is impossible to call a liquid homogeneous because the microscope fails to show structure.

All that can be said is that the particles in water, if not visible with lenses of the greatest possible angle for water, are probably not much greater than the 1/180,000 of an inch in diameter. Of course, it must be understood that changes in the limits will be observed when the refractive index of the particles differs very greatly from that of the fluid in which they are diffused, as is the case with As_2S_3 in water. It seems probable, therefore, that the phenomena observed in the cases of As_2S_3, and others which were mentioned, differ only in degree, and not in kind, from those in the cases of Sb_2S_3 and similar bodies, and from the opalescent liquids obtained in washing many precipitates.

*82. "The change proceeding in an acidified solution of sodium thiosulphate when the products are retained within the system." By A. Colefax, B.A., Ph.D.

Experiments were carried out in the following manner:—A certain volume of a solution of sodium thiosulphate, acidified with an equivalent quantity of acid, was enclosed in a small glass bulb from which the air had been displaced by carbon dioxide; several such bulbs were filled and placed in a bath at a fixed temperature, and at certain definite times after acidification the contents of a bulb was titrated by means of an iodine solution. The initial titration of the acidified sodium thiosulphate at the moment of acidification being known, the extent of chemical change is given by the iodine titration. The sulphurous acid resulting from the decomposition of thiosulphuric acid possesses a titration in terms of iodine the double of that of the undecomposed thiosulphuric acid. The possible sources of error are considered under the heads "Oxidation of sulphurous acid," "Titration complications" and "Incomplete saline decomposition." A further check is afforded by the determination of the acidity of the solution after the iodine titration is made. For a solution of sulphurous acid, there is a constant ratio between the iodine titration and the acidity of the solution after the iodine titration has been made. This value was determined for the particular iodine and ammonia

solutions, by means of a pure solution of sulphurous acid. Hence, whether or not the whole of the increase in iodine titration in the acidified solution of sodium thiosulphate is due to sulphurous acid can be ascertained by a determination of the two values, iodine titration and acidity developed after titration with iodine.

The author concludes that the change proceeding in an acidified solution of sodium thiosulphate when the products, viz., sulphurous acid and sulphur, are retained in the system, is a reversible one: a limit being reached a certain time from the time of acidification. The value of this limit is affected by (1) state of concentration, (2) ratio of the mass of acid relative to the sodium thiosulphate, (3) the nature of the acidifying acid, (4) the temperature. Sulphurous acid cannot prevent the decomposition of thiosulphuric acid. The presence of both products of the change in the system seems essential for the attainment of a limit value; for sulphurous acid, when initially present in the system at the time of acidification, has but a small effect upon the values expressing the extent of chemical change. A higher temperature favours the interaction of sulphurous acid and hydrogen or sodium thiosulphate, a secondary change which proceeds at lower temperatures with extreme slowness.

Spring's statement that sodium trithionate is formed by the interaction of iodine, sodium sulphite and sodium thiosulphate seems to be wrong; the author finds that in adding to a solution of iodine a mixed solution of sodium thiosulphate and sulphite no sodium trithionate is produced; the sodium sulphite is completely oxidised to sodium sulphate.

*83. "The action of sulphurous acid on flowers of sulphur." By A. Colefax, B.A., Ph.D.

Debus's statement that sulphurous acid has practically no action on sulphur is not confirmed. Sulphurous acid acts on flowers of sulphur at the ordinary temperature of the air, and produces thiosulphuric acid and a polythionic acid, probably trithionic acid. No pentathionic acid was found. According to Flückiger (*Jahresbericht*, 1863, 149), sulphurous acid gave, by its action on flowers of sulphur, thiosulphuric acid. The presence of a polythionic acid is proved by a comparison of the iodine titrations and the acidity titrations before and after the addition of iodine requisite for the iodine titration. It is thus shown that there is present a considerable quantity of an acid having no iodine titration, and which is not merely oxidised sulphurous acid. Qualitative tests point to the presence of thiosulphuric acid, or trithionic acid, or a mixture of the two. Not even in the dark is sulphurous acid without action on sulphur. A higher tempe-

rature (say 80—90° C.) favours the action of sulphurous acid on sulphur; water has no action on flowers of sulphur, either at ordinary temperatures or at this higher temperature.

84. "The α- and β-modifications of chlorobenzene hexachloride." By F. E. Matthews, Ph.D.

By the action of chlorine on chlorobenzene in presence of a dilute solution of sodium hydroxide, the author obtains a mixture of α- and β-chlorobenzene hexachloride, together with oily products which have not been investigated (*cf.* these Proceedings, 1890). The solid portion can be separated from the oily substances only with difficulty by pressure between filter-paper and washing with light petroleum. The α- and β-compounds are separated by means of steam distillation, the β-compound being much less readily volatile, and subsequent recrystallisation from alcohol, benzene or light petroleum.

α-$C_6H_5Cl_7$ is a colourless, crystalline substance closely resembling α-benzene hexachloride in its properties; it melts at about 146°, and can be sublimed if carefully heated, but if heated too strongly, or on warming with an alcoholic solution of potassium hydroxide, it is quantitatively resolved into 1 : 3 : 4 : 5-tetrachlorobenzene and hydrogen chloride; on boiling an alcoholic solution with zinc-dust, chlorobenzene is obtained.

β-$C_6H_5Cl_7$ is only obtained in small quantity: it is more stable than the α-compound and melts at about 260°; it is decomposed on heating either alone or with alcoholic potash, yielding the same tetrachlorobenzene as the α-substance.

Meunier's method of separating α- from β-$C_6H_6Cl_6$ by means of an alcoholic solution of potassium cyanide has been investigated, and has been found to depend on the conversion of the α-$C_6H_6Cl_6$ into 1 : 2 : 4-$C_6H_3Cl_3$, the cyanide playing the part of a weak alkali.

1 : 3 : 4 : 5-$C_6H_2Cl_4$ has been investigated, with the result that the author is of opinion that the melting point, 50—51°, assigned by Beilstein and Kurbatow, is correct, and that Otto and Ladenburg and Jungfleisch, who all give the melting point considerably lower, were dealing with impure material. The nitro-derivative, $C_6HCl_4(NO_2)$ (1 : 3 : 4 : 5 : 2), was prepared and found to melt at 23° (B. and K. 21—22°).

The action of bromine on benzene in the presence of alkali has also been studied, and is found to yield $C_6H_6Br_6$, the product being the same whether gaseous or liquid bromine was used. On mixing monochlorobenzene with bromine under water and allowing the mixture to stand for about a week, a considerable amount of pure chlorobromobenzene was obtained.

The author calls attention to a paper by Sachse (*Ber.*, **23**, 1363), in which Sachse shows that there are two positions of stability of the hexamethylene ring. According to Sachse's hypothesis, there should be two substances of the formula $C_6H_6Cl_6$ capable of existence, but *three* substances of the formula $C_6H_5Cl_7$, of which the two α-modifications would probably have very similar properties.

85. "The sulphochlorides of the isomeric dibromonaphthalenes. (I.)" By Henry E. Armstrong and E. C. Rossiter.

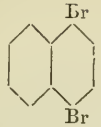
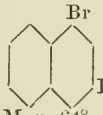
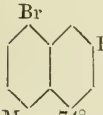
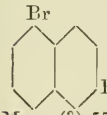
Many statements are on record with reference to the dibromonaphthalenes which are difficult to reconcile; the preparation of characteristic derivatives which could be made use of in distinguishing the various modifications is therefore of importance, and the more they are studied the more is this found to be the case; indeed, more than usual difficulty attends their investigation, as little or no reliance can be placed either on appearance or melting point, a slight impurity sufficing to produce most misleading changes in these; moreover, the separation of isomerides is made very difficult by their tendency to crystallise together, forming mixtures which simulate pure substances in a most remarkable manner. Unfortunately, also, at the high temperatures requisite to effect the hydrolysis of many of their sulphonic acids, slight decomposition takes place, in consequence of which an impure product is obtained.

Eight of the 10 possible dibromonaphthalenes have been prepared, only the 1 : 1′-$\alpha\alpha$- and the 2 : 3-$\beta\beta$-modifications being unknown. Five of the modifications are referred to in the present notice, viz.:—

1 : 4-Dibromonaphthalene, prepared by brominating naphthalene.
1 : 4′-Dibromonaphthalene, prepared from Guareschi's bromonitronaphthalene by reducing, diazotising &c.
1 : 3-Dibromonaphthalene, prepared by Meldola's method.
1 : 2′-Dibromonaphthalene, prepared by brominating β-bromonaphthalene.
1 : 3′-Dibromonaphthalene, prepared by the action of PBr_5 on the bromosulpho-acid obtained from the Dahl modification of β-naphthylaminesulphonic acid.

These dibromonaphthalenes are readily sulphonated by heating with twice their weight of H_2SO_4 (so-called 100 per cent. acid) on the water-bath until dissolution is complete; on adding potassium carbonate in slight excess to the moderately dilute solution of the sulpho-acid, the potassium sulphonate separates almost entirely from the liquid, and, after recrystallisation, is converted into sulphochloride.

The properties of the sulphochlorides are summarised in the following table:—

 M. p. 82—83°.	Yields only one sulphonic acid. SO_2Cl, prismatic needles; m. p. 120°.
M. p. 130°.	Yields only one sulphonic acid. SO_2Cl, prismatic needles; m. p. 175°.
 M. p. 64°.	Yields two sulphonic acids. α-SO_2Cl, prisms or highly refractive stumpy crystals; m. p. 157°. β-SO_2Cl, prismatic needles or long flexible plates; m. p. 128°.
 M. p. 74°.	Only one sulphonic acid isolated as yet. SO_2Cl, prismatic needles which, like the corresponding dichloro-derivative, become opaque on keeping; m. p. 113°.
 M. p. (?) 57°.	Only one sulphonic acid isolated as yet. SO_2Cl, massive prisms; m. p. 145°.

It was stated by Armstrong and Wynne, in 1886 (these Proceedings, p. 233), that when 1 : 3′-naphthalenedisulphonic acid is treated with bromine, it affords a dibromo-β-monosulphonic acid isomeric with that prepared by Jolin from naphthalene-β-sulphonic acid; this conclusion was based on the production from the acid by hydrolysis of a dibromonaphthalene of much lower melting point than the 1 : 4-modification, and altogether different from it in appearance: it is now found that the product of hydrolysis in question was impure 1 : 4-dibromonaphthalene, and it follows, therefore, that the acid from which it was derived is identical with Jolin's.

It is to be noted that whereas the dibromonaphthalenes all have higher melting points than the corresponding dichloronaphthalenes, no such relation obtains between the sulphochlorides of corresponding dichloro- and dibromo-naphthalene.

86. "The action of alcohols on sulphonic chlorides as a means of producing ethereal salts of sulphonic acids." By Henry E. Armstrong and E. C. Rossiter.

It is customary to prepare ethereal salts of sulphonic acids by the interaction of the silver salt and the bromide or iodide of a carbinol radicle. The authors find that several, but by no means all, of the dibromonaphthalenesulphochlorides may be converted into the ethereal salt by boiling with ordinary dehydrated alcohol; the 1 : 4-sulphochloride especially is remarkable for the readiness and completeness with which it undergoes this change, but a small proportion being hydrolysed and converted into sulphonic acid. The 1 : 4′-sulphochloride under similar conditions is entirely hydrolysed; its behaviour thus affords a striking contrast to that of the 1 : 4-compound, especially as both are β-sulphonic derivatives. The 1 : 2′-sulphochloride, which is an α-sulphonic derivative, also yields ethereal salts when boiled with alcohols, although in relatively small amount; this is a further proof that the formation of ethereal salts is not a function of the β-sulphonic radicle.

The peculiar behaviour of the 1 : 4-sulphochloride is of interest in connection with Heller's observation (these Proceedings, 1889, 121) that 1 : 4-dibromo-, dichloro- and chlorobromo-naphthalenes behave in a peculiar manner on treatment with SO_3HCl, being converted into sulphones, whereas isomeric compounds yield sulphonic acids as chief product.

It is proposed to study the behaviour of a number of typical sulphochlorides towards alcohols and sodium derivatives of alcohols.

*87. "The action of bromine on α- and β-bromonaphthalene." By Henry E. Armstrong and E. C. Rossiter.

It is well known that when naphthalene is submitted to the action of two molecular proportions of bromine, a product is obtained from which a considerable amount of 1 : 4-dibromonaphthalene may be separated without difficulty by crystallising from alcohol, leaving as major product a substance melting at 68—70°; numerous unsuccessful attempts have been made to determine the nature of this product, and although Magatti and also Guareschi have separated a small quantity of 1 : 4′-dibromonaphthalene from it, down to the present time its constitution has remained a mystery.

As β-dibromonaphthalene is formed in small quantity on brominating naphthalene, the action of bromine on this compound was first studied; it is found to afford 1 : 2′-dibromonaphthalene almost as sole product.

To determine the nature of the product of low melting point from naphthalene and two molecular proportions of bromine, it was sulphonated, and attempts were made to effect a separation by recrystallising the potassium salt of the resulting acid; as these were unsuccessful, sulphochloride was prepared: by crystallising this from benzene and from acetic acid, a considerable fraction of the product was ultimately recognised as the sulphochloride of 1 : 4-dibromonaphthalene. The residual sulphochloride melted at 107—110°; numerous attempts were made to purify this by crystallisation without success; it was hydrolysed at 260—270°, but the product had a low melting point and could not be identified; but on boiling it with alcohol, a considerable amount of the ethylic salt of 1 : 4-dibromonaphthalene-sulphonic acid was obtained. It was, therefore, evident that on brominating naphthalene much more 1 : 4-dibromonaphthalene is formed than is commonly supposed. Fresh attempts were then made to resolve the crude product melting at about 70° into its constituents by means of solvents. Eventually, on fractionally extracting it with light petroleum, it was found that the first separations from the last extracts melted at 115—125°: and on crystallising this product from alcohol, it melted at 129—130°, and was identified as 1 : 4′-dibromonaphthalene.

A small quantity of 1 : 4-dibromonaphthalene was obtained from the first extractions by petroleum; the rest of the product melted at 68—70°. On crystallising this latter from alcohol, a further separation of 1 : 4-dibromonaphthalene was obtained, but the residue still melted at 68—70°. However, by alternately crystallising this last product from petroleum and alcohol, it was gradually split up into 1 : 4- and 1 : 4′-dibromonaphthalenes, the melting point of the residue always remaining constant at 68—70°.

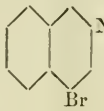
From these results it is concluded that the substance melting at 68—70° is a mixture of 1 : 4- and 1 : 4′-naphthalene, and from the weights obtained of these it is concluded that the 1 : 4-dibromonaphthalene constitutes about four-fifths and the 1 : 4′- one-fifth of the mixture.

No 1 : 3-dibromonaphthalene was obtained. As a mixture of 1 : 4- and 1 : 3-dichloronaphthalenes is obtained by the action of chlorine on naphthalene, the production of the 1 : 4- and 1 : 4′-compounds by the action of bromine would seem to be an indication of a great difference between the action of chlorine and bromine on naphthalene; but such is not the case. The formation of the dichloronaphthalenes is preceded by that of a comparatively stable tetrachloride, but no such compound is produced by the action of bromine; probably a highly unstable dibromide is first formed, which is at once resolved into hydrogen bromide and bromonaphthalene, and the latter is then

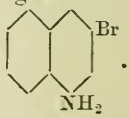
further acted on. Experiments, of which an account will be given later on, show that when chloronaphthalene is chlorinated results are obtained very similar to those obtained on brominating bromonaphthalene.

*88. "The action of bromine on a mixture of ortho- and paranitro-α-acenaphthalide." By Henry E. Armstrong and E. C. Rossiter.

Meldola, in 1885 (Trans., pp. 497—518), described two series of compounds derived, one from brominated α-acenaphthalide, the other from nitrated acenaphthalide; the former was converted by nitration into nitrobromacenaphthalide, from which the amido-group was eliminated, and the resulting nitrobromonaphthalene was reduced, a bromonaphthylamine being thus obtained, which—judging from previous observations—must necessarily be the compound of the formula



Nitrated acenaphthalide was known to be a mixture of the ortho- and para-derivatives; by brominating the mixture Meldola obtained a single product which he supposed to be derived from the *para*-constituent, and, therefore, he regarded the bromonaphthylamine obtained by eliminating the amido-group and then reducing as the isomeride of that prepared from bromacenaphthalide, viz., as

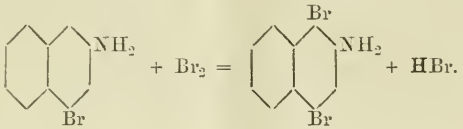


From the bromonaphthylamines from the two sources, Meldola prepared dibromonaphthylamines, from which he then prepared dibromonaphthalenes, obtaining in this way a modification melting at 74° from each source. Some time after the appearance of his paper (*cf.* these Proceedings, 1886, 172), he was led to modify his views of the constitution of the compounds he had obtained in consequence of the discovery by Stallard that the bromophthalic acid which Meldola prepared by oxidising one of his dibromonaphthylamines was derived from an α- and not from a β-bromonaphthalene; Meldola, therefore, suggested that the one amine was the compound $NH_2 : Br : Me = 2 : 4 : 1'$, and the other the compound $NH_2 : Br : Me = 1 : 3 : 3'$ or $1 : 3 : 2'$.

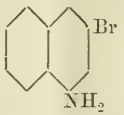
Wishing to prepare the 1 : 1'-dibromonaphthalene, the authors proceeeded to repeat Meldola's work, as the argument which he made use of appeared to be a sound one, and there was, therefore, reason to

think that the dibromonaphthalene which he had obtained starting from brominated acenaphthalide was the 1 : 1′-modification; that obtained from the other source the authors were inclined to expect would prove to be the 1 : 2′-modification, which is known to melt at 74°.

On preparing the two bromonaphthalenes in accordance with Meldola's directions, products were obtained, however, which both melted at 82—83°, the identity of which with 1 : 4-dibromonaphthalene was placed beyond doubt by conversion into the sulphochloride melting at 118—120° and the ethylic sulphonate melting at 156—157°. The production of 1 : 4-dibromonaphthalene from the bromonaphthylamine prepared from nitrated parabromacenaphthalide is easily understood, thus—



Its production from a bromonaphthylamine of the formula



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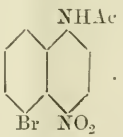
however, is clearly impossible; but it was conceivable that a heteronucleal derivative is formed on brominating paranitracenaphthalide, viz.:—



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In this case, the bromonaphthylamine obtained on eliminating the NHAc group and reducing should be convertible into 1 : 1′-dibromonaphthalene; according to Meldola, it yields 1 : 3-dibromonaphthalene, but he was led to form this conclusion only by the appearance and melting point of the product. The authors have prepared the dibromonaphthalene in question, and have proved it to be the 1 : 3-compound, as stated by Meldola, by converting it into the two sulphochlorides melting at 127° and 157° characteristic of this modification; and by completely reducing the bromonaphthylamine in question they have obtained β-naphthylamine.

There appears to be but one explanation possible of these results, viz., that when a mixture of ortho- and para-nitracenaphthalides is brominated, the ortho-compound—not the para-, as Meldola supposed

—is alone attacked, and that consequently the same nitrobromonaphthalene is obtained on displacing the acetamido-group in nitrated parabromo-α-acenaphthalide, and in the product of the action of bromine on a mixture of the ortho- and para-nitro-derivatives of α-acenaphthalide.

Meldola, although struck with the remarkable similarity of the two series of compounds which he prepared, was led to notice certain differences: thus he obtained bromonaphthylamines melting, the one at 71·5°, the other at 62°; but the authors find that both products melt at 72°; and that the dibromonaphthylamines prepared from them melt at the same temperature, viz., 106°. Messrs. Miers and Pope have examined a number of the pairs of products, and report that corresponding compounds are not only identical in form but also in optical properties, and as no case is on record of different substances being alike both morphologically and optically, there can be no doubt of the correctness of the explanation now advanced.

*89. "Camphrone, a product of the action of dehydrating agents on camphor." By Henry E. Armstrong and F. S. Kipping.

The action of concentrated sulphuric acid on camphor appears to have been first examined by Chautard; it was subsequently studied by Fittig, Schwanert, and Kachler, all of whom agree in stating that under suitable conditions an oily product, having a strong peppermint odour, is formed, isomeric with acetophorone, $C_9H_{14}O$, which consequently has figured in chemical literature under the name *camphorone*. The various statements regarding the properties of this substance, however, are by no means confirmatory, Fittig stating that it boils at 204—205° and that it has a relative density of 0·939 at 12°, whereas Schwanert gives 230—235° as its boiling point and 0·9614 at 20° as the relative density.

Armstrong and Miller noticed the presence of a substance having properties similar to those of the product obtained by means of sulphuric acid among the products of the action of zinc chloride on camphor; but attempts which they made to isolate a definite substance from their crude product were unsuccessful.

It appeared probable that, with the aid of the improved methods of treating ketonic compounds now known, it would be possible to separate the characteristic constituent from the crude oil, and this has proved to be the case.

On treating the fraction boiling at 238—242° of the oil prepared by means either of sulphuric acid or of zinc chloride with phenylhydrazine, a mixture of a crystalline hydrazone with dark-coloured, oily products is obtained; the purified hydrazone crystallises in yellowish

plates and melts at about 108°. By boiling it in alcoholic solution with ferric chloride and muriatic acid, an oil is obtained which yields a hydrazone identical with that from which it was prepared; on distilling this oil, the thermometer rapidly rises to 245°, the greater part of the liquid passing over at 245—247°. On treatment with hydroxylamine, the oil is converted into a hydroxime which crystallises in long prisms melting at 85—86°, of which the acetyl derivative melts at 69—70°.

The determination of the composition of these compounds presents considerable difficulty; analyses of the oil gave the following results:—

Carbon, per cent.....	80·84	80·88
Hydrogen „	8·13	8·14

numbers which agree satisfactorily with the formula $C_{10}H_{12}O$. But in numerous analyses of the hydroxime, the carbon was found to vary from 72·4 to 72·8 per cent.; hydrogen from 7·8 to 8·0 per cent.; and nitrogen from 8·6 to 8·9 per cent.: these values do not agree with those required by a compound of the formula $C_{10}H_{12}N(OH)$ except the nitrogen values (C = 73·6, H = 7·27, N = 8·6). The acetyl derivative of the hydroxime gave similar results. The hydrazone was found to contain 12 to 12·2 per cent. of nitrogen, the calculated value for $C_{10}H_{12}N_2HPh$ being 11·8. Evidently it is necessary to make a more complete study of the compound to place its composition beyond doubt, especially as the formula $C_{10}H_{12}O$ is a very remarkable one.

On oxidising the oil with nitric acid, it yields an acid which crystallises well.

Obviously the substance is one of considerable interest, and its further investigation is likely to throw light on the still open question as to the structure of camphor. As the yield even of the crude product is small, and the preparation of the pure substance is a matter of considerable difficulty, it appears desirable to make this preliminary announcement, now that workers are becoming so numerous in this field.

*90. Metaxylenesulphonic acids (II)." By G. T. Moody, D.Sc.

In a previous communication (Proceedings, 1888, p. 77), the author has described the preparation of 1 : 2 : 3-metaxylenesulphonic acid, and has called attention to the fact that only the 1 : 3 : 4-acid is formed on direct sulphonation of the pure hydrocarbon. Attempts to prepare the symmetrical 1 : 3 : 5-sulphonic acid have not yet met

with success, the sulphonation of 1 : 3 : 4-acetmetaxylid failing to give the required substitution.

Acetmetaxylid (1 : 3 : 4) is readily sulphonated when heated for some time at 140° with 1½ times its weight of 20 per cent. anhydrosulphuric acid, and on boiling the solution after the addition of water, metaxylidinesulphonic acid [$Me_2 : NH_2 : SO_3H = 1 : 3 : 4 : 6$] is obtained. It crystallises from water, in which it is only very sparingly soluble, in well-formed, slender needles, insoluble in alcohol and other common solvents; it does not change at 290°, and when heated to a higher temperature, decomposes without having previously melted. The sodium salt, $C_6H_3Me_2NH_2SO_3Na,H_2O$, is exceedingly soluble in water and crystallises in flat plates.

On diazotising the acid and subsequently boiling the solid product with dehydrated methylated spirit, ethoxymetaxylenesulphonic acid [$Me_2 : OEt : SO_3H = 1 : 3 : 4 : 6$] was obtained. The sodium salt of the acid crystallises in long, slender needles which effloresce when exposed to the air; the sulphochloride crystallises from light petroleum in beautiful orthorhombic plates, melting at 56°; the sulphonamide separates from dilute alcohol in small, white scales or flat needles which melt at 169—170°.

When the diazo-product is boiled with with bromhydric acid, the corresponding bromoxylenesulphonic acid [$Me_2 : Br : SO_3H = 1 : 3 : 4 : 6$] is formed. It crystallises in long, slender needles, and does not melt at 270°, but at a considerably higher temperature, melts with decomposition. The sodium salt agrees with the description given by Weinberg (*Ber.*, **11**, 1062), who obtained it on bromination of a dilute aqueous solution of barium 1 : 3 : 4-metaxylenesulphonate; but the sulphochloride obtained by the author, which crystallises in splendid, oblique prisms, melts at 2° higher (62—63°), whilst the sulphonamide melts at 5° lower (189°) than found by Weinberg. The melting point of the sulphonamide agrees with that given by Sartig (*Annalen*, **230**, 335), who prepared it by sulphonating metaxylidine, and subsequently replacing amidogen by bromine. It thus appears that both xylidine and acetxylid give the same acid on sulphonation, and that the displacement of hydrogen in the amido-group by acetyl does not lead to any change in the position taken up by the sulphonic group.

*91. "The action of propylene bromide on the sodium derivatives of ethylic acetoacetate and ethylic benzoylacetate." By W. H. Perkin, Jun., Ph.D., F.R.S., and James Stenhouse.

The product from ethylic acetate is a mixture of ethylic acetylmethyltrimethylenecarboxylate and ethylic methyldiacetyladipate.

The former is found to yield a well-crystallised hydroxime (m. p. 153—155°); when boiled with water, it is gradually converted into acetoisobutyl alcohol. Ethylic methyldiacetyladipate is decomposed on distillation into an oil which is a mixture of at least two compounds, as, when hydrolysed, it yields dimethyldihydropentenedicarboxylic acid, together with dimethyldihydropentene methyl ketone.

Ethylic benzoylmethyltrimethylenecarboxylate and several of its derivatives are also described in the paper.

92. "Derivatives of tetramethylene." By W. H. Perkin, Jun., Ph.D., F.R.S., and W. Sinclair, B.Sc.

By the action of bromine in presence of phosphorus on tetramethylenecarboxylic acid, the authors have obtained an almost quantitative yield of the monobromo-derivative. They describe its methylic salt, and the corresponding hydroxy-, acetoxy- and ethoxy-acids. By acting on the chloride of the acid with zinc methyl and ethyl, they have prepared tetramethylene methyl and ethyl ketones, of which they also describe the reduction products.

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Die optische Anomalien der Krystalle, von R. Brauns. Leipzig 1891.

Analyse der Fette und Wachsarten, von R. Benedikt. 2te Auflage Berlin 1891.

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Tabellarische Uebersicht der künstlichen organischen Farbstoffe, von G. Schultz und P. Julius. Berlin 1891.

Anleitung zur Untersuchung der für die Zuckerindustrie in Betracht kommenden Rohmaterialien, Producte, Nebenproducte und Hülfssubstanzen, von R. Frühling und J. Schultz. 4te Aufl. Braunschweig 1891.

Jahresbericht über die Fortschritte in der Lehre von den Gährungs-Organismen, von A. Koch. Erster Jahrgang 1890. Braunschweig 1891.

Elektro-Metallurgie: die Gewinnung der Metalle unter Vermittelung des electrischen Stromes, von W. Borchers. Braunschweig 1891.

Die galvanische Metallplattirung und Galvanoplastik, von W. Pfanhauser. Wien 1890.

Ausführliches Handbuch der Photographie. 2te Auflage. Band I. Heft 3; Die Photographie bei künstlichem Licht, von J. M. Eder. Halle a.S., 1891.

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